

JOURNAL

OF THE

OIL AND COLOUR CHEMISTS' ASSOCIATION



Vol. 44, No. 11

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November, 1961

TRANSACTIONS AND COMMUNICATIONS

Further Papers from the May Conference on "Physics in Surface Coatings" :

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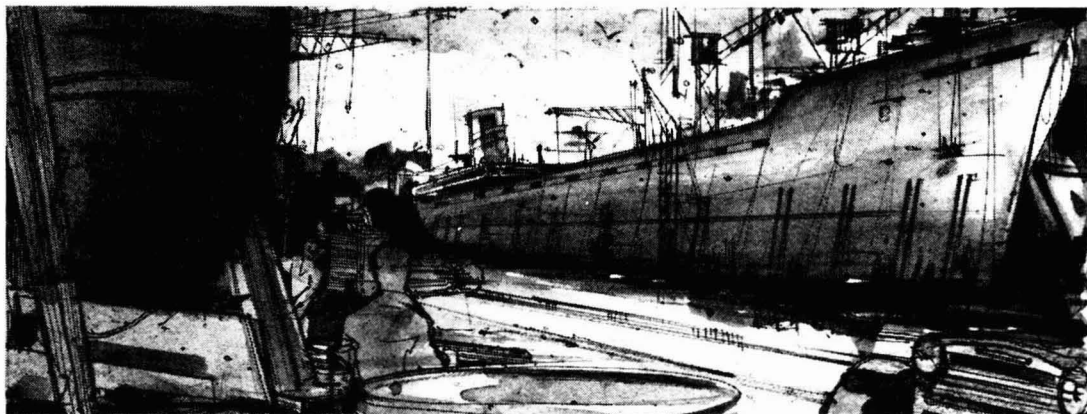
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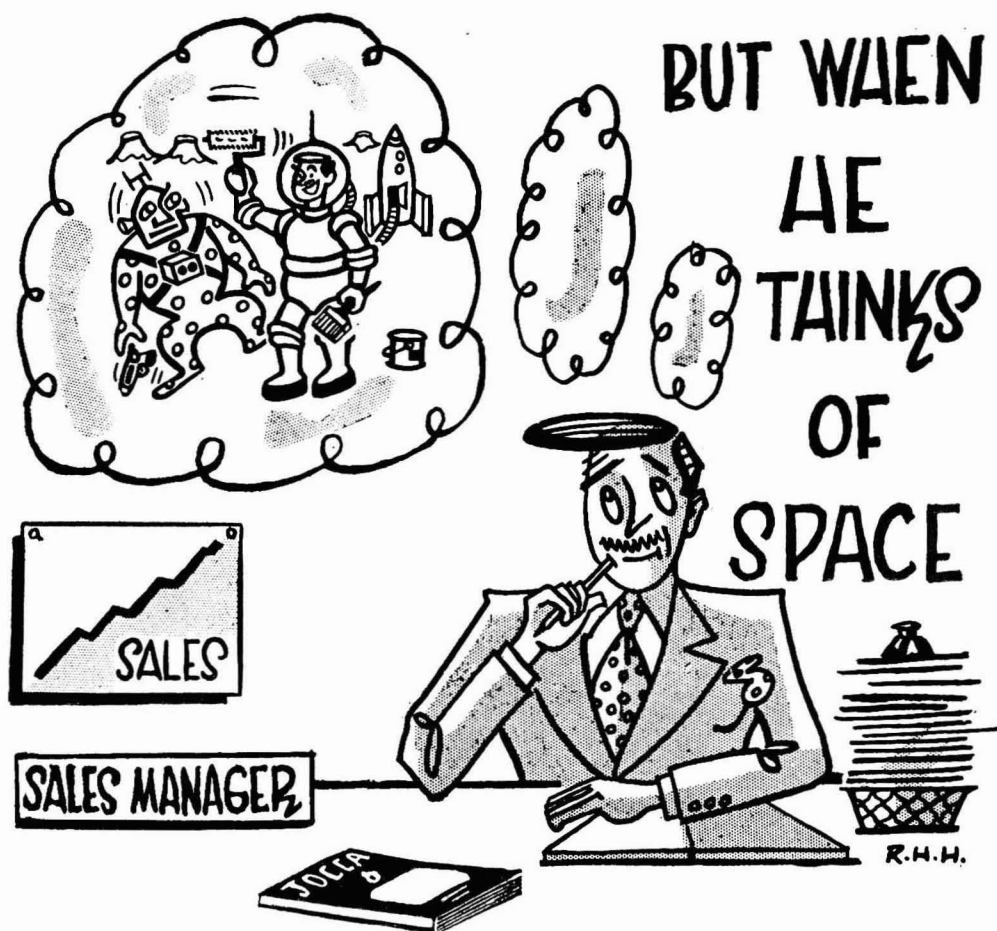
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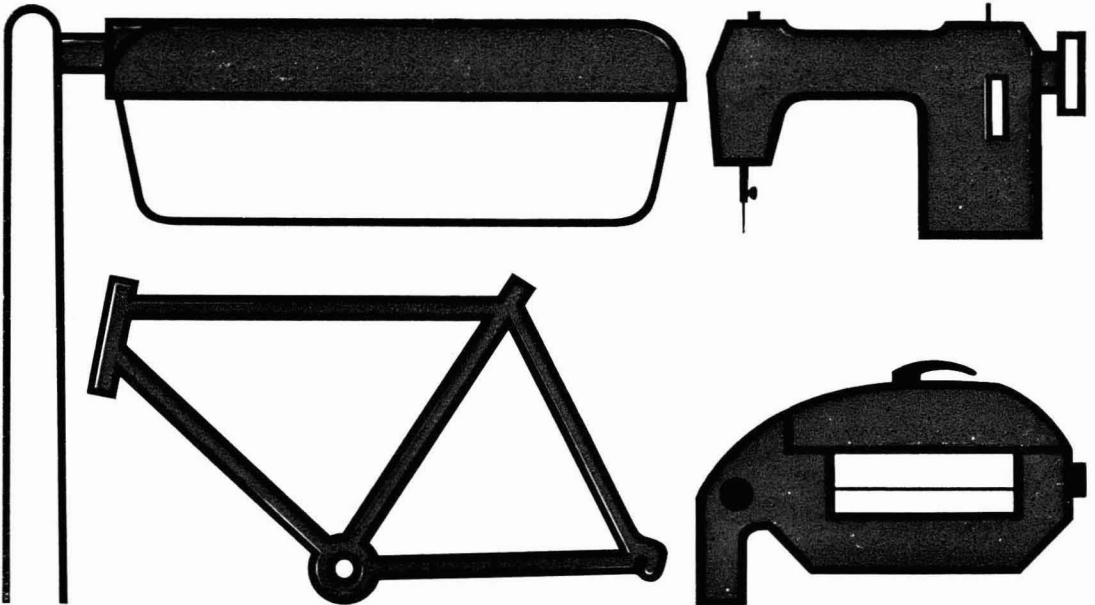
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Adverse are the Uses of Synonymy

By NEIL R. FISK

HOMONYMY — *Using the same name to denote different things.*

SYNONYMY — *Having different names for the same thing.*

These two diseases are pandemic in the industries supplying the manufacturers of paints and printing inks. Resins, oils, pigments, solvents, chemicals, plant, and apparatus—all of them are riddled with synonymy and all of them are troubled with homonymy. Users of works of reference and collected lists will be only too well aware that this sometimes leads to a good deal of duplication, confusion, and exasperation.

How much better it would be for everybody if "ester gum" were not extended to cover a pentaerythritol ester of polymerized rosin, if "polyoxyethylene" were used for only one class of substances, and if "ethoxylates" were eschewed altogether!

The main work of compiling *Fisk's Paint Year Book and A-Z Buyers' Guide* was completed some time ago—with a few loose ends still to be tied up or cut off according to whether or not the firms concerned do eventually reply to letters—but now I am engaged in "decompiling" the examples of homonymy and cross-referring the examples of synonymy that have "crept in". And the number of these was, at first, disturbingly large. It is much smaller already, but the work must continue until homonymy is to all intents and purposes eliminated and synonymy reduced to a system of cross-references. This operation has led understandably to a big increase in these, which now number almost as many as the whole collection of product headings in a reference book recently brought out. The product headings in *FPYB & BG* are nearly four times as many as the cross-references.

That homonymy and synonymy would exist in any collection of lists of paint raw materials I knew before I started, but their extent in width and depth was unexpected, and accounts for my being not quite ready to invite orders for the book—though a fair number have in fact come in, some from overseas. It'll be all the better for the eradication of those two diseases homonymy and synonymy, and users making quick references in the future will be glad they didn't get something half cooked.

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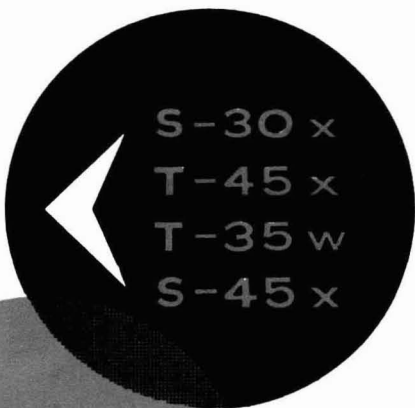
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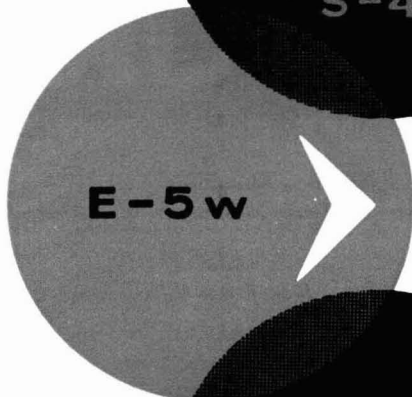
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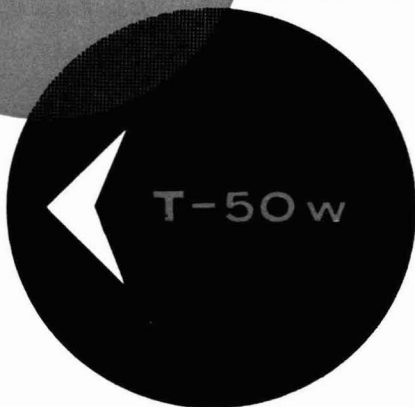
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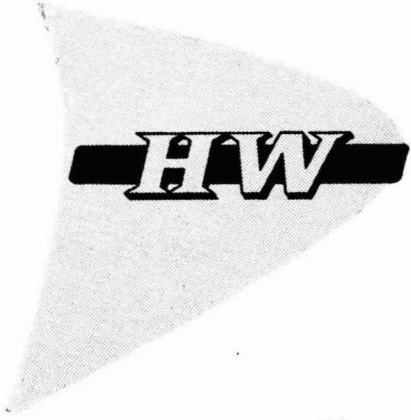
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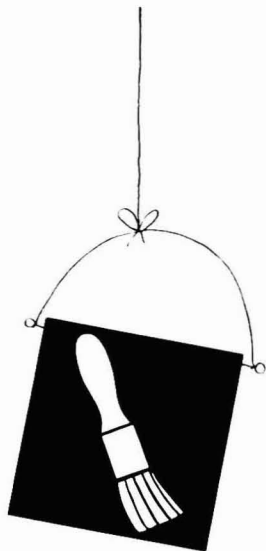
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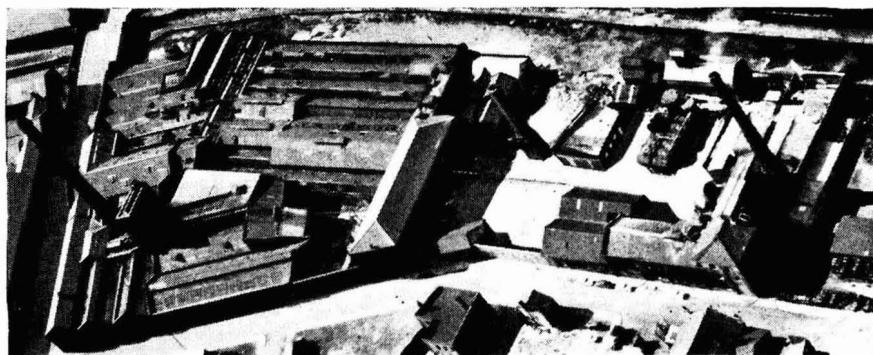
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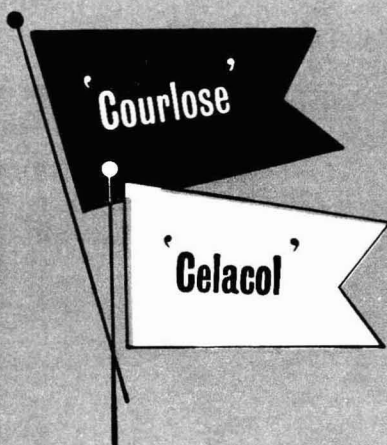
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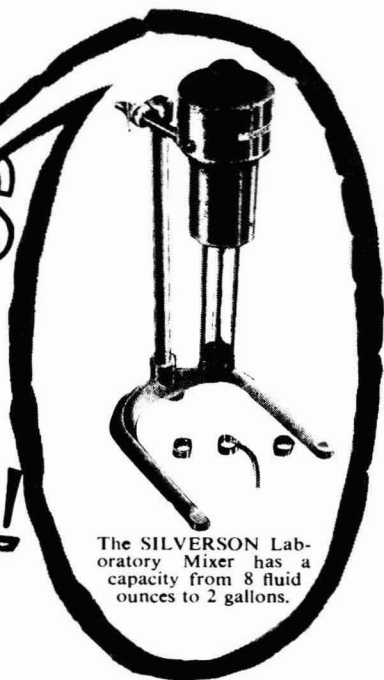
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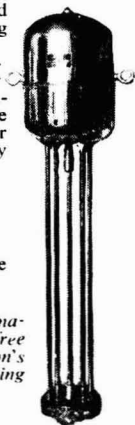
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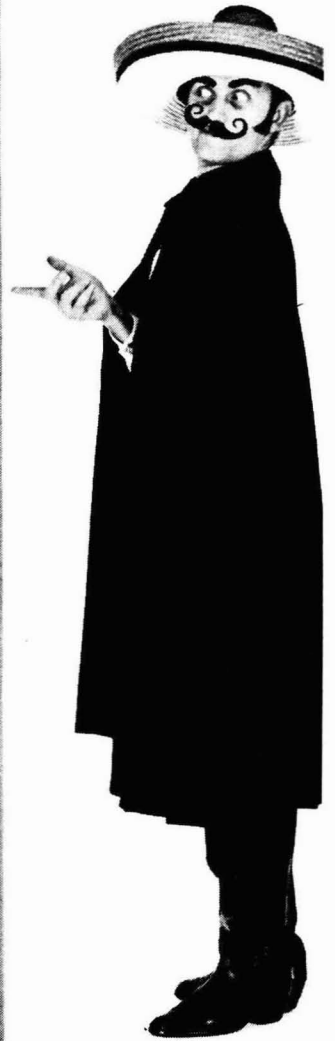
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TRANSACTIONS AND COMMUNICATIONS

Absorption of Paint Media into Porous Substrates

By G. W. MACK

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Summary

As part of a study of problems associated with painting on porous substrates, a series of tests is carried out to measure the rate of absorption, by three types of bricks, of twelve liquids used as paint media and of three paints. The results show general agreement with theory in that, for a given type of brick, the amount of liquid absorbed in a given time is a function of the surface tension divided by the viscosity of the liquid. However, simple tests of the behaviour of paint when applied as a thin film by brush to the surface of the bricks show that other factors have an important influence. A general discussion outlines the further factors requiring investigation.

INTRODUCTION

The term "porous substrate" covers a wide range of materials used in building, such as brick, stone, plaster, cement products, wood, asbestos boards and fibre building boards. The pores in these materials generally form a three-dimensional labyrinth of channels, which vary considerably in cross-section along their length. Liquids that wet the surfaces are pulled into the pores by capillary forces. Because water in the pores is of importance in the behaviour of building materials and in soil mechanics, the behaviour of water has been studied extensively, but little information is available for other liquids.

When paint is applied to a porous surface, the medium is absorbed to a greater or lesser extent, leaving pigment or emulsion particles mainly on the surface. If absorption is rapid, it may be difficult or impossible to spread the paint evenly and the levelling of brushmarks may be unsatisfactory. In extreme cases, so much of the medium is removed that under-bound pigment is left on the surface and defective adhesion results. Subsequent undercoats and finish coats may also lose enough of the medium to show uneven colour or gloss, uneven finish, and poor weathering qualities. Such abnormally absorbent surfaces are said by the painter to be "hot" or to show high suction.

This paper deals with a study of the absorption of a variety of liquids by three types of bricks, to demonstrate what properties of the liquids govern absorption and whether any of the liquids offer special advantages for paint formulation. Some pigmented materials and three commercial paints were also examined to find to what extent pigments reduce the absorption.

Bricks

MATERIALS

Several hundred specimens of porous material were required for this study. In order to avoid the difficulties involved in the preparation of specimens, it was decided to use bricks. Three types of bricks were chosen which were reasonably consistent in properties, and of approximately equal porosities, but with different pore size distributions.

TABLE I
VOLUME OF PORES AND PORE SIZE DISTRIBUTION IN BRICKS BY MERCURY PENETRATION METHOD

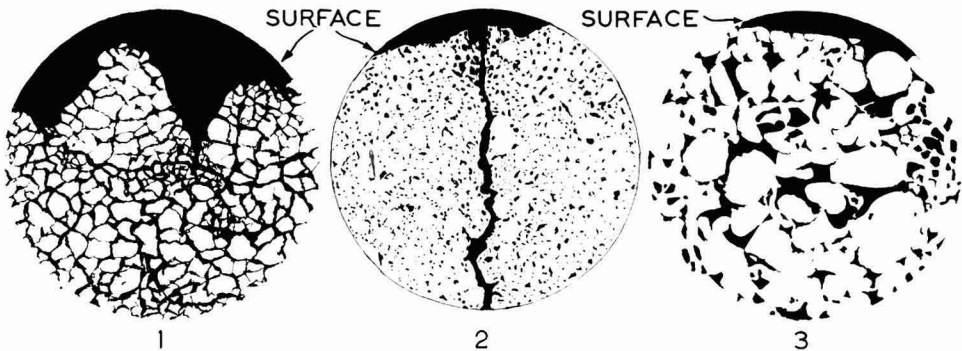
Type of brick	Total porosity (% vol.)	Porosity (% vol.) in the size range				
		> 25 μ	25-10 μ	10-2 μ	2-0.1 μ	< 0.1 μ
Pressed red facing brick† ..	32	7	9	8	2	6
	30	8	14	7	2	0
Leicester red wirecut‡	25	6	3	13	4	0
	23	4	1	11	4	3
Sand-lime brick grade A (i)* ..	31	13	2	2	5	9
	26	9	2	2	6	7

†Hammill Brick Co. Ltd.

‡Ibstock Brick & Tile Co. Ltd.

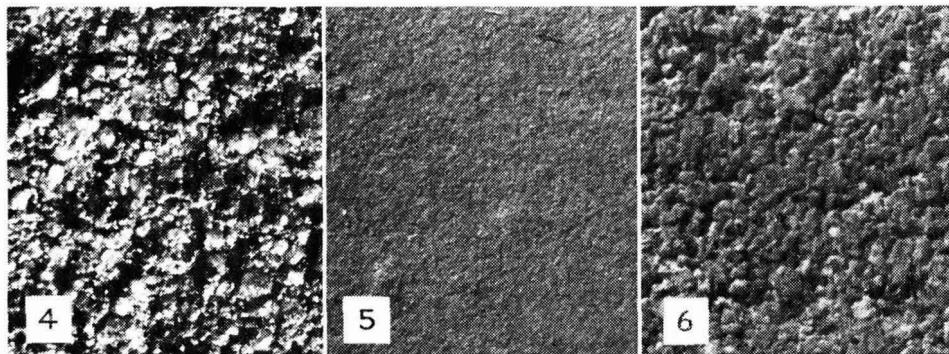
*Stonehenge Brick Co. Ltd.

The pore size distribution of the most and the least porous bricks in each of three batches of twelve bricks, determined by the mercury penetration method¹, are given in Table I. In this method, mercury is forced into the brick under gradually increasing pressure. The amount penetrating the brick is measured, and pore sizes are calculated on the assumption that the pressure required to force the mercury into a pore is inversely proportional to the radius of the pore. The pore size distribution can therefore be inferred, subject to the limitation that a pore that is larger than any of those leading into it will be measured with those of a size equal to that of its largest entrance. This method needs supplementing by microscopical examination of sections, to give some indication of the conformation of the pore structure and tracings from such photomicrographs are given in Figs. 1-3. It should be recognised,



PHOTOMICROGRAPHS OF SECTIONS OF HAMMILL BRICK (FIG. 1), LEICESTER RED BRICK (FIG. 2) AND SAND-LIME BRICK (FIG. 3) Magnification $\times 15$

however, that a two-dimensional section may be misleading as regards connections between the pores. The surface appearance of the bricks is shown in Figs. 4-6. The sand-lime bricks are considered by painters to show high suction, the others moderate suction.



SURFACE OF HAMMILL BRIC (FIG. 4), LEICESTER RED BRICK (FIG. 5) AND SAND-LIME BRICK (FIG. 6) Magnification $\times 2\frac{1}{2}$

Liquids

The liquids were chosen to cover a wide range of viscosities and surface tensions, and a wide range of chemical compositions. The details are given below and in Table II.

The following seven homogeneous liquids were examined:

Distilled water.

White spirit to B.S. 245.

Glue size to B.S. 647, described as 100 per cent bone glue of 100 gram strength. One pound of the glue was soaked in one pint of cold water for twenty minutes and then made up to two gallons with boiling water. It was allowed to cool and was used four hours after the addition of the boiling water.

Glue size, similar to that above, allowed to stand for eighteen hours after making. Some thickening of the solution occurred during this time.

Raw linseed oil to B.S. 243, diluted with an equal volume of white spirit.

Linseed stand oil, viscosity diluted with an equal volume of white spirit.

Commercial cellulose paste, made by sprinkling two ounces of the powder into $1\frac{1}{2}$ gallons of cold water and allowing to stand for twenty-four hours with occasional shaking before use. The shorter periods used in practice did not give a sufficiently homogeneous solution.

Two emulsions were examined:

Emulsion A, an emulsion of unplasticised p.v.a. with a particle size of less than 0.5μ , containing only the protective colloids for manufacture and let down to a solids content of 20 per cent by volume.

Emulsion B, similar to Emulsion A, but with a particle size of $1-2 \mu$.

Three suspensions were examined, as follows:

Monastral Fast Blue BNVS dispersion (0.1 per cent by volume), of a particle size of about 0.5μ , prepared by diluting the commercial dispersion with distilled water.

Limewash, made by slaking Buxton quicklime overnight, straining through a fifty-two mesh sieve and diluting to a concentration of 20 per cent by volume. This material is thixotropic and exhibits plug flow in capillary tubes.

Limewash, similar to the above, but with an addition of 1 per cent by weight on the water of an anionic dispersing agent, *Dispersol T*, to disperse the lime particles. In this condition, the material behaves as a near-Newtonian fluid.

Commercial Paints

Three commercial paints of reputable brands were also examined, an emulsion paint and an oil-bound water paint (A), neither of which was difficult to apply except to surfaces of exceptionally high suction, and an oil-bound water paint (B) that was not easy to apply to surfaces of even moderately high suction.

METHODS

All determinations were done at 65 per cent relative humidity and 64° F; the materials were brought to equilibrium with this environment before use.

Absorption

Many methods for the study of absorption use some form of cap, fixed to the surface of the absorbent and connected to a narrow tube. The cap and tube are filled with the liquid to be absorbed. The volume absorbed is measured by the movement of the liquid in the narrow tube. These methods were unsatisfactory with the more viscous liquids under investigation, partly because of the difficulty in filling the apparatus without trapping bubbles, and partly because of the uncertainty of the time of start of the experiment.

A simpler method was therefore used. The $8\frac{3}{4}$ in. \times $2\frac{1}{2}$ in. face of the brick was dipped for a period to a depth of $\frac{1}{4}$ in. in a 10 in. \times 9 in. tray of the liquid under investigation, removed, wiped immediately and weighed. The same surface was used for repeated determinations at different times, but if any appreciable deposit was formed on the surface, a check test was done to see whether the removal of this deposit at intervals affected the longer-term readings. With limewash no great difference seemed to result, but with the emulsions the difference was marked.

The advance of liquid into the bricks is substantially uniform across the centre, but rather greater at the edges. The results, therefore, depend to a slight extent on the dimensions of the specimen, hence expression of the results as c.c./cm.² is best avoided and the results have been expressed in c.c. absorbed per brick.

Where the formation of a surface deposit affected longer-term readings, an alternative method was used. A glass funnel, sealed to the surface of the brick with an epoxy resin cement, was connected by tubing to a burette, as shown in Fig. 7. The funnel and burette were filled with liquid to just below the surface

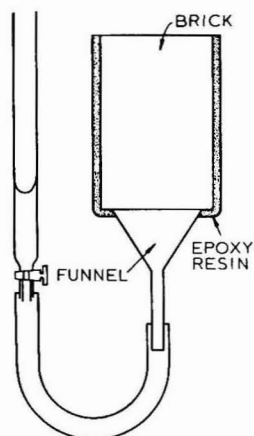


FIG. 7. APPARATUS FOR DETERMINING ABSORPTION BY BRICKS

of the brick. The burette was raised initially to bring the liquid surface into contact with the brick and then moved periodically to keep the liquid in it level with the absorbing surface of the brick. The volume absorbed could be read at any time from the graduations of the burette. This method was satisfactory with emulsions, but not for some of the more viscous materials. Because there is some lateral spread from the funnel, the results are not fully comparable with those obtained by dipping, but serve to investigate choking of the pores.

The results are expressed in c.c.

Viscosity

Except for the thixotropic limewash, the liquids studied approximated to Newtonian fluids and the viscosity was determined using glass U-tube viscometers to B.S. 188.

Surface Tension

The present studies are largely concerned with the advance of liquids into air-dry solids, but it is not possible to determine the surface tension and contact angle in the pores themselves, without unjustifiable assumptions. In order to specify the properties of the liquids, therefore, the product of the surface tension and the cosine of the contact angle was determined from measurements of the rise of the liquid when it maintained a steady value for five minutes in a glass capillary tube. The tube had been cleaned with chromic acid, water and finally with acetone, and then dried by passing air through it. With the more viscous liquids, the rise may be substantially less than in a wetted tube.

Absorption from Brush Applied Coats

Further tests were made to determine whether measurements of the rate of absorption from bulk liquids were related to the time taken for the media to be absorbed from brush applied coats. This was measured by observing the "50 per cent matting time", *i.e.* the time that elapsed from the start of application before an estimated 50 per cent of the surface ceased to show a specular reflection from the film of liquid applied to it. The choice of this

percentage avoided the effects of small areas of exceptionally high absorbency, which rapidly became matt, as well as areas of exceptionally low absorbency, where matting was delayed. At the onset of matting, it should be noted that the capillary forces pulling liquid into the brick are beginning to be opposed by back suction, but no earlier stage is susceptible to exact timing.

The paint was applied to the surface in a natural coat by a professional painter and the mean of four determinations on the $8\frac{3}{4}$ in. \times $2\frac{1}{2}$ in. faces of the brick was calculated.

ABSORPTION PROCESS

Theoretical

The rise of liquids in porous bodies has been treated in soil mechanics largely on an experimental basis and by Washburn by the use of a model of a bundle of capillary tubes of varying sizes. It is not proposed to elaborate these treatments here, since they are readily available in books on soil mechanics² or in Washburn's paper³. Both lead essentially to a relation:

$$V = k \left(\frac{\sigma \cos \theta}{\mu} \right)^{\frac{1}{2}} t^{\frac{1}{2}} \dots \dots \dots (1)$$

where V is the volume absorbed by unit area at time t from the start of the process,

k is a constant, depending on the pore structure of the particular porous body,

σ is the surface tension,

θ is the contact angle, and

μ is the viscosity.

It has been demonstrated that a relation of this kind holds for the movement of water in soil or for the advance of liquids into packed pigment powders^{3, 4, 5}, as long as the liquid advances on a plane "wave front". While it may not be applicable to the simple form of dipping test used in this paper, particularly where the supply of liquid is interrupted at intervals for the specimen to be weighed, it does suggest a basis on which to examine the experimental results. The results of the first investigation were therefore examined to see whether a relation in the form:

$$V_t = K \left(\frac{\sigma \cos \theta}{\mu} \right)^{\frac{1}{2}}$$

would adequately represent the data. Taking logarithms of both sides, this becomes:

$$\log V_t = \log K + \frac{1}{2} \log \left(\frac{\sigma \cos \theta}{\mu} \right)$$

The validity of this expression can be conveniently examined by plotting $\log V_t$ against $\log (\sigma \cos \theta / \mu)$. If the relation holds, then a linear graph with a slope of 0.5 should be obtained.

Effect of the Surface Tension and Viscosity of the Liquid

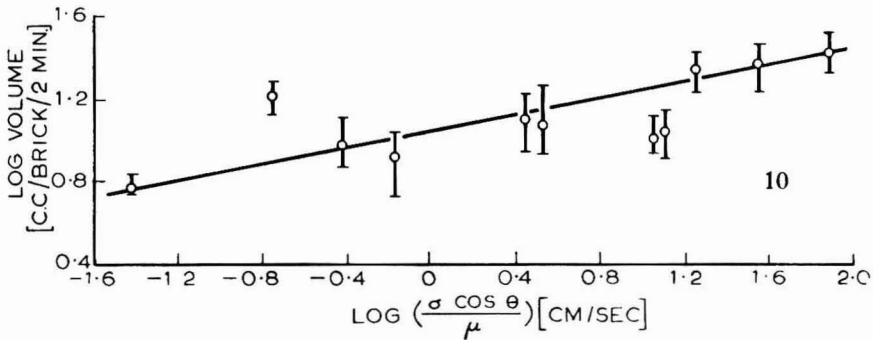
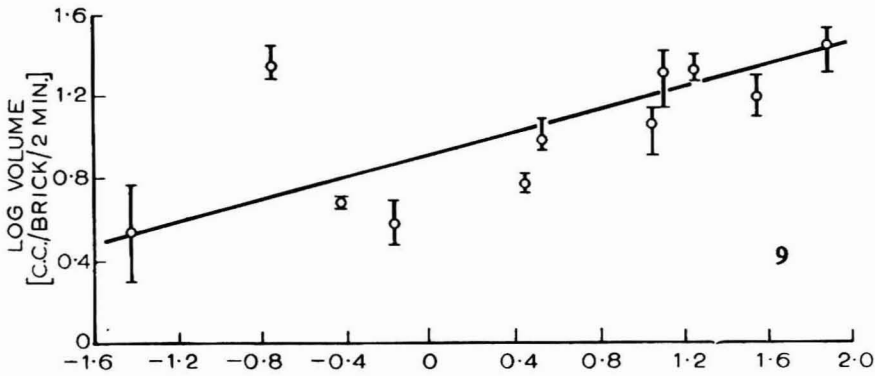
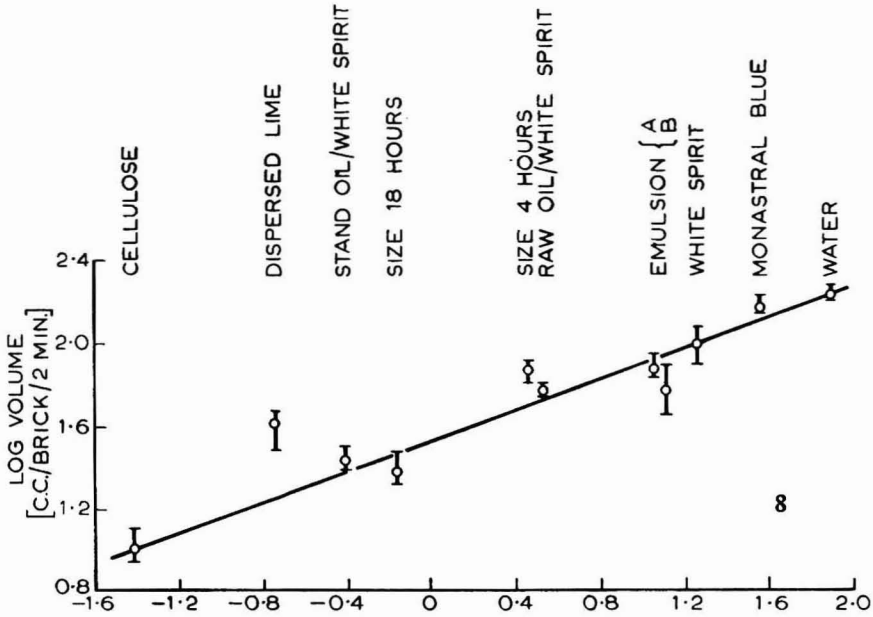
Since it is not possible to remove absorbed liquid completely from the pore structure of bricks, single bricks could not be used for successive determinations with a variety of liquids. Even with a wholly volatile liquid such as water, redeposition of soluble matter in the pores as the liquid evaporates can introduce variations. It was therefore necessary to reduce the variability between bricks, by taking the mean volume of liquid absorbed in a given time by ten bricks of each kind. Both the mean and the range of these ten observations are used in plotting the results.

TABLE II
SOME PROPERTIES OF THE LIQUIDS USED IN THE STUDIES OF ABSORPTION

Liquid	Surface tension $\sigma \cos \theta$ (dyne/cm.)	Viscosity μ (centipoise)	$\frac{\sigma \cos \theta}{\mu}$ (cm./sec.)	Density (g./c.c.)
Distilled water	70.3	0.90	78.2	0.997
Monastral blue dispersion ..	39.1	1.08	36.2	1.000
White spirit	24.4	1.37	17.8	0.824
Emulsion A	30.1	2.73	11.0	1.04
Emulsion B	36.4	2.88	12.6	1.04
Raw oil/white spirit	27.0	7.8	3.45	0.877
Size (4-hour)	24.0	8.3	2.90	1.015
Size (18-hour)	31.0	62.4	0.50	1.015
Stand oil/white spirit	27.5	70.5	0.39	0.894
Dispersed limewash	41.2	233	0.18	1.24
Cellulose soln.	29.8	758	0.039	1.001

The logarithms of the volumes absorbed in two minutes are plotted against $\log(\sigma \cos \theta/\mu)$ in Figs. 8, 9 and 10. It is possible to fit straight lines, the slopes of which differ from the theoretical value of 0.5, and vary for each kind of brick, viz.,

Type of brick	Slope of graph
Hammill	0.37
Leicester red	0.28
Sand-lime	0.21



VOLUME ABSORBED PLOTTED AGAINST $\left(\frac{\sigma \cos \theta}{\mu}\right)$ FOR HAMMILL BRICKS (FIG. 8), LEICESTER RED BRICKS (FIG. 9) AND SAND-LIME BRICKS (FIG. 10)

A number of the readings show appreciable departures from this relationship. Notably, the dispersed limewash is always significantly ($P > 0.01$) above the line. The emulsions and the size solutions tend to be below it, but only with the four-hour size on the Leicester red bricks are these departures significant statistically.

Absorption from Limewash

The possibility of pigment preventing absorption by choking the pores of the bricks is of considerable interest. Individual absorption of ten bricks at two minutes are given in Table III for water, thixotropic and dispersed limewash,

TABLE III
VOLUMES (C.C.) ABSORBED IN TWO MINUTES

	Hammill			Leicester red			Sand-lime		
	Water	Limewash		Water	Limewash		Water	Limewash	
		Thixo-tropic	Dis-persed		Thixo-tropic	Dis-persed		Thixo-tropic	Dis-persed
	172	44	31	32	20	20	29	16	18
	183	55	36	31	16	21	31	15	19
	171	47	42	27	16	21	28	18	16
	162	49	46	22	19	19	26	19	19
	161	52	43	22	19	27	26	18	17
	170	45	45	22	16	22	25	17	15
	187	44	42	23	24	21	29	17	14
	179	44	45	20	22	22	33	14	18
	190	45	39	34	28	24	22	20	16
	166	47	41	34	24	22	21	21	14
Mean	174	47.0	41.0	26.7	20.4	22.0	27.0	17.5	16.6
Standard error of mean	3.2	1.0	2.0	2.5	1.7	0.8	1.7	0.9	0.6

together with the means and the standard errors of the means. Statistical examination of these results shows that there is no significant difference between the thixotropic and the dispersed limewash, but that there is a significant difference ($P = 0.05$ or better) between the volumes absorbed from water and from either limewash. It is evident that the pigment has a proportionately greater effect in retarding the absorption of the liquid medium by Hammill bricks than it has on either of the other two kinds. A much greater reduction

would in fact be achieved with a simple liquid of equal surface tension and viscosity.

The Rate of Absorption of Paint Media

Plots of $\log V$ against $\log t$, illustrating the absorption of the various liquids on Hammill bricks, are shown in Figs. 11 and 12. Similar results were obtained

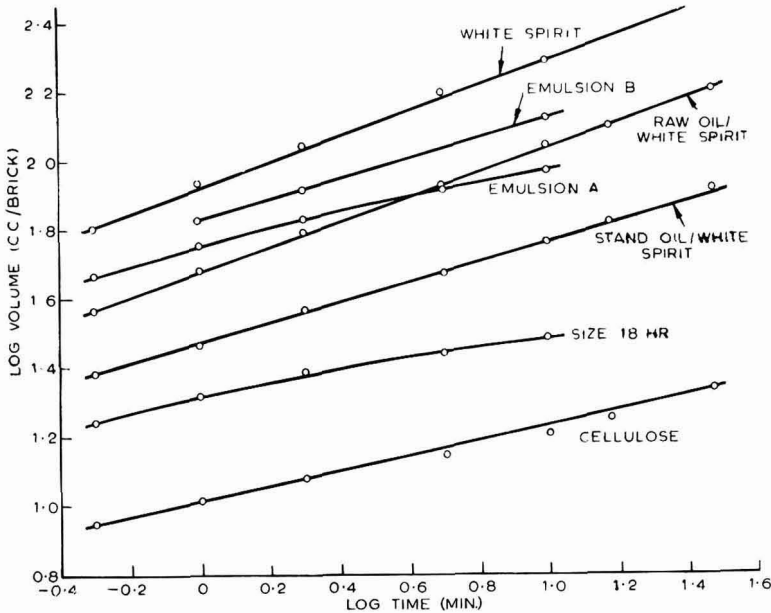
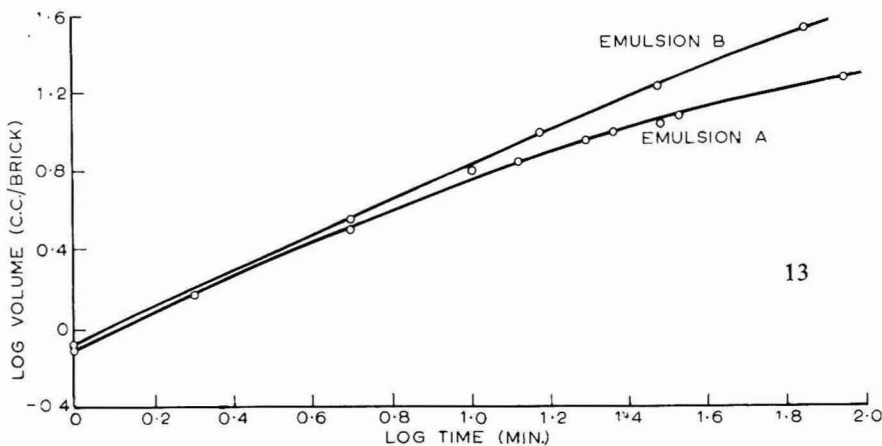
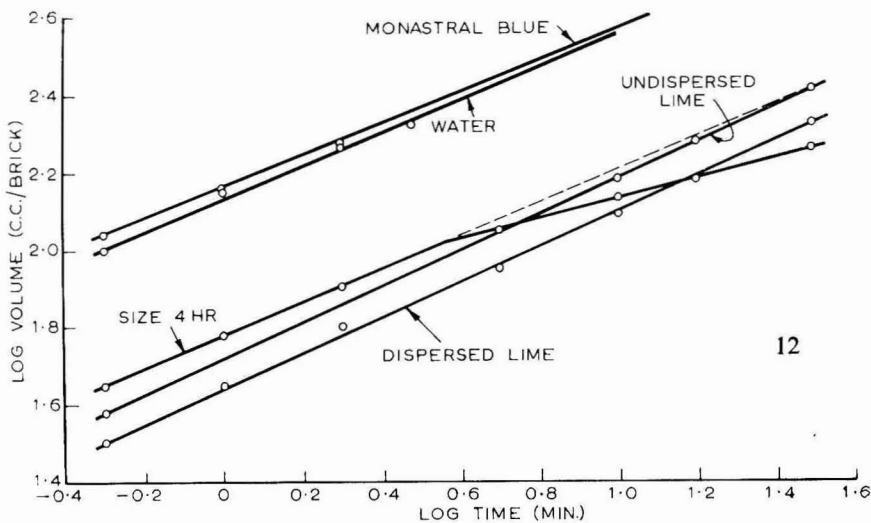


FIG. 11. ABSORPTION OF LIQUIDS BY HAMMILL BRICKS

on the other bricks. Theoretical treatment of the process would be difficult because of the interruptions in the absorption process, during which some redistribution of the liquid in the pores may occur. It was found, however, that with simple liquids, and with limewash, the interrupted absorption at the end of thirty minutes or one hour was within the range of figures obtained where undisturbed absorption had taken place.

This was not true of the emulsions, where long absorption results in the formation of a slimy and later a horny membrane; the removal of this membrane by wiping at intervals may well explain the difference. For this reason, only short-term absorptions of the emulsions are shown on the graphs. Absorption of these materials was also examined by the funnel method on Leicester red bricks, in order to allow uninterrupted absorption (Fig. 13). Both graphs depart from linearity which shows that there is an appreciable clogging of the pores, particularly with Emulsion A, but this is not apparent until after the first five or ten minutes. It is the earlier stages, immediately after application, that are of interest in the painting of porous substrates. The initial slopes for the various liquids are given in Table IV. In order to provide some estimate of variability, the values for water are given for six separate bricks of each variety.



ABSORPTION OF LIQUIDS BY HAMMILL BRICKS (FIG. 12), AND OF EMULSIONS BY LEICESTER RED BRICKS—FUNNEL METHOD (FIG. 13)

The variability is such that fine distinctions cannot be drawn without much more data, but it can be seen that the absorption of water, white spirit, the emulsions and the pigmented materials form one set with slopes not significantly different, while the absorptions of the stand oil/white spirit mixture, the solutions of size and cellulose generally have a significantly lower slope.

The Choice of Paint Media

In so far as better performance may be expected from paints on surfaces of high suction if the rate of absorption is reduced, these results enable the media of low absorption rate to be selected. The factors on which the choice depends are the surface tension, the viscosity and the slope of the $\log V/\log t$ graphs. It must be realised, however, that only a limited reduction in the rate of absorption is achieved in this way. A hundred-fold reduction in the ratio of

TABLE IV
INITIAL SLOPES OF LOG V/LOG *t* GRAPHS FOR DIFFERENT LIQUIDS

Liquid	Type of brick		
	Hammill	Leicester red	Sand-lime
Water	0.36, 0.38, 0.38 0.38, 0.40, 0.41	0.38, 0.48, 0.46 0.43, 0.44, 0.50	0.28, 0.28, 0.28 0.28, 0.32, 0.33
Monastral blue dispersion ..	0.39	0.47	0.27
White spirit	0.38	0.48	0.28
Emulsion A	0.28	0.50	0.35
Emulsion B	0.38	0.50	0.32
Size (4-hour)	0.42	0.21	0.19
Raw oil/white spirit	0.37	0.41	0.23
Size (18-hour)	0.25	0.31	0.24
Stand oil/white spirit ..	0.31	0.25	0.14
Limewash .. dispersed	0.45	0.45	0.36
thixotropic	0.45	0.45	0.32
Cellulose soln.	0.23	0.28	0.28

$\sigma \cos \theta / \mu$ will only reduce the absorption by, at most, a sixth. In the same way, the choice of a material with a log V/log *t* slope of 0.25, instead of 0.50, would almost halve the amount of liquid absorbed in ten minutes. In both cases the reductions are rather small, but if they can be associated with a proportionate increase in the time during which the paint can be easily brushed about on the surface, they could make a material difference to the ease of painting. Of the media investigated, this approach would lead, according to the type of paint being formulated, to the selection of the cellulose or size solutions or the stand oil, these being in fact recognised as being of value on surfaces of high suction.

However, even with the most viscous solutions used, the amount absorbed per brick is high in relation to the liquid content of wet paint films. The mean absorption of the cellulose solution in two minutes for the ten bricks examined was 10.3, 3.5 and 5.9 c.c. per brick for Hammill, Leicester red and sand-lime bricks respectively. A normal paint coverage of 60 yd.²/gal. corresponds, however, to only 1.6 c.c./brick, only about half of which is liquid. Other factors must be operative in practice in order to explain the longer working time that is in fact obtained. In the absorption from bulk liquid, the only other factor so far examined is the choking effect of the particles, which seems to operate for limewash and the emulsions, but not to an extent that would seem adequate to explain the discrepancy.

Absorption from Paint

It is conceivable that considerably lower rates of absorption may arise in paints themselves from a combination of all the effects of viscosity, surface tension and the presence of pigment and emulsion particles. Similar absorption tests, with a rather longer absorption time of ten minutes, were therefore made using a commercial emulsion paint and two commercial water paints. The results are given, together with those for a cellulose solution, in Table V. The slopes of the $\log V/\log t$ graphs were also estimated by taking the absorption at two time intervals (Table VI).

TABLE V
ABSORPTION FROM BULK PAINT AND CELLULOSE SOLUTIONS

	Mean absorption (c.c./brick/10 min.)		
	Hammill	Leicester red	Sand-lime
Emulsion paint	3.7	3.5	4.3
Water Paint A	5.4	6.2	8.7
Water Paint B	27.0	20.8	14.5
Cellulose solution	16.8	4.8	13.3

TABLE VI
SLOPES OF $\log V/\log t$ CURVES FOR BULK PAINT AND CELLULOSE SOLUTIONS

	Slope		
	Hammill	Leicester red	Sand-lime
Emulsion paint	0.19	0.52	0.48
Water Paint A	0.22	0.50	0.24
Water Paint B	0.35	0.56	0.42
Cellulose solution	0.23	0.28	0.28

The volume absorbed from the good paints is nearly constant with all three bricks and appreciably less than that from the cellulose solution or from the less satisfactory Water Paint B. The discrepancies between the volumes absorbed from the bulk paints and the volumes available from the thin films applied in painting, however, still remain.

The Behaviour of Thin Films

The behaviour of thin films was examined, as already described, by determining the matting time of brush coats of the four-hour size and the cellulose solutions. The weight of the film applied by brush, the time that would be required to absorb this liquid from bulk (calculated by extrapolation from graphs such as Figs. 11 and 12) and the matting time are given

in Table VII. In spite of the very short matting times, the painter experienced little difficulty, since there was no build-up on the surface to cause increased brush drag. The observed matting times are longer than those calculated for the absorption, but both are very short and the differences might arise if a few seconds were required to wet the surface or by a slowing down in the later stages of absorption. Further, the estimates of the time of absorption from bulk represent large extrapolation. Critical examination of the value of the absorption results with these solutions is therefore not possible. Similar experiments were carried out with three commercial paints. The paints and scrapings from an applied paint film, which had become matt, were dried and an estimate of the amount of liquid to be lost before matting occurred was obtained in this way.

TABLE VII

COMPARISON OF OBSERVED MATTING TIME WITH CALCULATED TIME OF ABSORPTION FROM BULK

Solution	Cellulose			Size (4-hour)		
	Hammill	Leicester red	Sand-lime	Hammill	Leicester red	Sand-lime
Application rate (g./brick) (yd. ² /gal.)	3.3 23	1.0 77	2.1 37	5.7 13	1.1 70	2.5 31
Time to absorb this quantity from bulk (sec.)	1.5	1.0	1.0	1.0	0.2	0.2
Time for 50% matting (sec.)	16	15	12	1-2	14	3

In the determination of matting times, it was observed that, with Water Paint B, on the Leicester red and sand-lime bricks there was an appreciable increase in brush drag within two or three seconds and that this drag rapidly increased until the paint became unworkable. With the distemper A and the emulsion paint on these bricks, appreciable increase in brush drag occurred within ten seconds, but thereafter it increased more slowly. The painter described the Leicester red bricks as being of moderate suction and the sand-lime bricks as being of high suction. The Hammill bricks were not regarded as being of high suction in spite of their high absorbency from bulk. This may be because the rough texture of the surface necessitated heavy application of paint, so that pools of liquid left in the hollows of the brick surface remain shiny for long periods. The thinner layers of paint on salient areas rapidly became matt, but the bristles of the brush seemed to ride over a hard film on these areas without introducing any great amount of drag. Joining up was facilitated by the existence of the pools of wet paint in the hollows. The comparison of absorption from bulk and matting times is given in Table VIII. The differences are large and it must be concluded that absorption of medium from bulk is of only limited value as a guide to the performance of thin films on the surface. A possible explanation may lie in the formation of a relatively impermeable cake of pigment and emulsion, on which the paint can be brushed.

TABLE VIII
BEHAVIOUR OF COMMERCIAL PAINTS

Paint	Emulsion paint			Water Paint A			Water Paint B		
	Hammill	Leicester red	Sand-lime	Hammill	Leicester red	Sand-lime	Hammill	Leicester red	Sand-lime
Application rate in determining matting time . . (g./brick) (yd./gal.)	4.1 24	2.4 42	2.6 38	5.2 26	3.1 43	4.2 32	4.2 29	2.1 58	3.1 39
Liquid to be lost to matting (c.c./brick)	1.3	0.8	0.9	0.9	0.5	0.7	0.6	0.3	0.5
Time to absorb this quantity from bulk (sec.)	2.4	35	24	0.2	3.4	0.1	0.1	0.1	0.1
Time for 50% matting (sec.)	270	75	75	480	90	40	130	18	15

Behaviour on Filter Paper

In order to examine the extent to which there are differences in the ease with which the three paints can build up a membrane and reduce the absorption of the medium, experiments were carried out by attempting to filter the paints through a Whatman No. 1 filter paper in a Buchner funnel under a suction of 12 cm. of mercury. The emulsion paint and Water Paint A lost no water after the first few drops, whereas the less satisfactory water paint (B) lost water steadily, until the volatile content of the resulting cake of pigment was the same as that observed on a paint which had become matt on a brick. Similar results were obtained in filtration under suction using a rather coarser filter paper, Whatman No. 4. Lateral spread into a single filter paper or spread into a lightly compressed pile of filter papers gave comparable results. Liquid from the good paints failed to spread or penetrate appreciably, while liquid from the less satisfactory material (B) spread or penetrated rapidly.

Tests of this kind are useful in the routine testing of paints and in the development of new formulations. But the emulsion paint and Water Paint A did not filter, spread or penetrate in these tests and the tests were therefore not helpful in improving the quality of these paints further, in the hope that they will then be able to deal with surfaces of the highest suction met with in practice.

DISCUSSION

The process by which a paint becomes matt on a surface may be conveniently considered as occurring in three stages. In the first stage, the liquid paint is applied to the surface by brush and any pigment structure tends to be broken down by shear between the surface and the bristles of the brush; simultaneously, some medium begins to be drawn into the pores. At this stage, the particles of pigment and emulsion (if present) may be considered as moving freely in the liquid and exerting little resistance to the movement of the medium.

In the second stage, pigment or emulsion particles begin to clog the narrower parts of the pores and may in fact be packed rather more tightly together

than in absorption from bulk liquid because of the action of brushing. It seems possible that as a result of this clogging action, a layer of liquid, only a little more viscous than the original paint, may remain above the clogged pores (much as the liquid does when the paint is filtered under suction), and this may only slowly lose its liquid. This would explain why after an initial increase in brush drag in the first ten seconds, further increase in brush drag is relatively slow with the good materials. The inability of Water Paint B to choke even a filter paper is paralleled by the high rate of absorption (Table V) and by the rapid increase in brush drag when bricks are painted. One of the factors in the efficiency of this choking process is no doubt the particle size grading and the charge on the particles, but the fact that the choking is much more marked on Hammill bricks absorbing from limewashes than on the other two types of bricks indicates that the nature of the substrate has a marked influence.

In the third stage, sufficient liquid will have been lost to cause the particles throughout the paint film to become closely packed enough to form a structure of their own. As long as this structure is saturated with medium, it will exert only a viscous resistance to the passage of the medium. Continuing the removal of liquid will mean, however, that eventually the liquid surface recedes within the porous structure, and the formation of liquid menisci in the paint film at the outer surface will allow back-suction to occur. The shiny surface of the paint will have become matt at this stage, which is, of course, beyond that at which brushing can be effectively continued. If there were no changes due to evaporation of volatile constituents or to chemical reactions, the final stage would be one in which the liquid medium is shared in such a way that the suction of the pigmented coating counterbalances the suction of the substrate, but a true equilibrium may not be reached before the paint dries.

Where an unpigmented medium, such as size, is applied to a porous substrate, neither the clogging process, nor the third stage, which involves competing pore systems of pigment and substrate, applies. The liquid is sucked into the pores until the formation of menisci at the outer surface opposes further entry; some redistribution between pores of different size may subsequently occur. The behaviour of the next coat of paint will depend on the success the previous coat has had in choking the pores of the surface and on the pore structure of the previous coat at dryness. If there are few open channels through which absorption can occur, the dry first coat will prevent undue absorption of the liquid part of the next coat.

Further work will be required to see how far choking of the surface pores depends on the pigment grading and pigment charge and whether it is affected by the act of brushing. In addition it will be necessary to obtain surfaces for routine tests less variable than the present bricks, but more searching in their action than filter paper.

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REFERENCES

1. Watson, A., May, J. O., and Butterworth, B., *Trans. Brit. Ceram. Soc.*, 1957, **56**, 37.
2. Taylor, D. W., "Fundamentals of Soil Mechanics" (New York: Wiley, 1948).
3. Washburn, E. W., *Physical Review*, 1921, **17**, 273.
4. Eley, D. D., and Pepper, D. E., *Trans. Faraday Soc.*, 1946, **42**, 697.
5. Stubbaker, M. L., and Snow, C. W., *J. Phys. Chem.*, 1955, **59**, 973.

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DISCUSSION

THE CHAIRMAN, DR. V. G. W. HARRISON, said that he had been impressed by the parallel which existed between the various porous systems. Although his knowledge of painting bricks was limited, he did know something about applying films to paper, and he was struck by the parallel between decorating buildings and paper; it was an excellent example of the way in which the different studies could fertilise each other. He considered that the great value of such conferences was that those engaged in one field of research could gain useful ideas from people working in other fields.

DR. V. R. GRAY suggested that the mercury penetration technique for pore distribution was rather remote from practical considerations. The contact angle was unknown and mercury was a liquid unlikely to be used for paint, and he felt that the method was rather inappropriate for that type of investigation. Pore size distribution could be obtained by incremental absorption of the liquids studied in an evacuated system. It would perhaps be necessary to work under vacuum, allow the liquid to penetrate under increments of vacuum and consider pore size with each increment.

The lack of agreement with Washburn's equation, he continued, could be explained by two effects. First, the air inside the brick would create a back pressure, thus lowering the rate of absorption; this could be eliminated by prior evacuation. Secondly, blocked pores or "ink bottle" pores would reduce absorption rates in the later stages of the experiment. It should be possible to explain the experimental results theoretically by taking these effects into account. The brick could probably be evacuated completely in order to eliminate the back pressure and a proper mathematical relation might then be possible.

MR. MACK replied that pore size measurements by any method was rather inaccurate. He thought that the more serious problem in the mercury penetration technique was that, if there were a space with one or two large entrances, the whole space tended to behave as if it were a very large pore. Of the methods available, the mercury penetration method was generally one of the best, but it needed also sections and microscopic examination. It was a quite useful method for presenting a broad view of the situation. There was also quite a variety of methods using increments of liquids, which were allowed to enter by means of vapour pressure. These were useful on some building materials but, generally speaking, all the absorption on these bricks occurred at between 98 and 100 per cent moisture content. When liquid entered the brick, it was not really possible to determine exactly where it went. Some idea of pore size might be gained, but the author did not feel very optimistic that other methods would improve on the mercury penetration method.

At the Building Research Station calculations had been made on the basis of the Washburn theory, but a good correlation was not often obtained. He said that Dr. Gray had raised two points to indicate why the Washburn equation might not be true, both of them valid, but he did not feel that back pressure was serious.

MR. G. PHILLIPS agreed with Dr. Gray that the back pressure was important in the penetration of capillaries. Dr. Bruyne, work on the wetting power of adhesives, had calculated the back pressure and it appeared to be quite considerable. He asked what was the water content of the various bricks used by the author and if they differed

appreciably, and further whether a high water content affected the penetration of water-incompatible materials. Some of the oils were compatible with water, *i.e.* they were water-based.

MR. MACK replied that back pressure was much less serious than in the work referred to, because the liquids advancing were much more viscous than the air which was escaping, and that air could readily escape through the back of the brick, which was not sealed. Thus in the case of Leicester red bricks, the back pressure with water is less than one per cent of the suction causing the liquid to advance.

At 65 per cent R.H. and a temperature 64°F the water content of the bricks was very low, often of the order of 1 per cent, and usually considerably less. Conditioning took a long time, and in no instance was the period less than one month. There was probably a certain amount of water on the surface, but it would be present in practice.

MR. D. R. GRAY asked why the author had not experimented with paints, because it was paint that was applied to the surfaces, and in that case the effect of thixotropy and pigmentation would be taken into account. He wondered if it mattered to practical paint manufacturers whether water or linseed oil penetrated bricks, for they were asked to produce primers. He enquired whether the author had done any work on typical paints.

MR. MACK stated that he and his colleagues had begun with a simple liquid and had intended to graduate to more complex ones. They had included a simple emulsion, and passed to commercial emulsions and distempers. They had used various primers, often based on linseed oil, but it was the oil absorption which had made him avoid those at this early stage of the work. The absorption of oil from a primer was extremely important. If an adhesion test was made on an ordinary white lead primer applied to a sand-lime brick, the adhesion obtained would be very low. All the oil would be absorbed by the background. It was a very poor paint for a high suction surface.

Mr. Mack said that he had not entered the field of the thixotropic measurement. It was mentioned in the paper that they thought the action of the bristles of the brush, another complication not fully considered, might prevent the absorption of medium by forcing the pigment particles into a close pattern. However, the surface of the brick had been brushed while it was wholly in contact with the paint and the absorption had been found to increase by about 50 per cent.

It seemed that with thixotropic paints the action of the brush, in breaking down thixotropy, could be important, but was more likely to increase absorption. The author said that he did not know whether there was also any mechanical forcing of liquid into the pores.

MR. W. H. NEWELL enquired about mechanical stress and the penetration of medium into the brick.

MR. MACK replied that viscosity, surface tension, etc., had been determined, although the problem was perhaps not fully dealt with in the paper. With pigmented materials the pigments would be to a greater or lesser extent "strained-out". In the case of lime wash the liquid which entered the pores was almost entirely water.

For some of the simple linseed oils, stand oils, *etc.* the ordinary standard tests of acid saponification and iodine values were made, and it was found that the Hammill brick did not affect any change in these analyses. The Leicester red brick, which was slightly alkaline, changed the acid value from about 2.4 to 1.6. The sand-lime brick was much more effective, which he did not think was very surprising. After contact with the brick the acid value would decrease from 2.4 to 0.1 or 0.2; the iodine value would not suffer any material change.

Some of the oils were treated with ground sand-lime brick; absorption by the sand-lime brick had then been determined but no change was found. The viscosity of the oils did not presumably change materially. However, over the general field of the materials considered he thought that the linearity or non-linearity of the absorption curve was a better indication of any progressive changes.

There was another aspect of change which might be occurring differently in the brick from in bulk. The viscosity of size would increase if the materials were left for long enough. He had always wondered whether there was the likelihood of gel formation in a brick pore quicker than in the bulk liquid.

The Wetting, Adhesion and Penetration of Surface Coatings on Wood

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Summary

A review is given of the thermodynamics of wetting and spreading on solids and it is shown that the linear relation established by Zisman, between liquid surface tension and the cosine of contact angle for low energy solids, can be used to calculate changes of energy during the application of surface coatings to wood, even when the liquids are in the region of complete spreading. Typical values for spreading coefficient of surface coatings on wood are calculated. The influence of roughness is correctly described by Wenzel's equation if properly interpreted. Roughness effects are shown to be small on planed wood surfaces.

Problems of adhesion are complex and difficult to reduce to quantitative terms. The adhesion failures of films on wood are frequently cohesion failures in the film or in the wood. The penetration of surface coatings is studied microscopically and its importance for film behaviour discussed.

FUNDAMENTALS OF WETTING

The first process of applying a surface coating material to any solid surface is the wetting of that surface by a liquid. This process will be considered in some detail. The fundamental equations for the energy changes taking place during a wetting or spreading process are:—

$$\Delta A = \Delta A_s + \Delta A_B \dots\dots\dots (1)$$

$$\Delta A_s = \sum \gamma_{ik} \Delta \sigma_{ik} \dots\dots\dots (2)$$

$$\Delta A_B = \sum m_l g \Delta h_l + \sum m_n \Delta (v_n^2) \dots\dots\dots (3)$$

where ΔA is the change in Helmholtz free energy of the system (negative for a spontaneous process).

ΔA_s is the change in surface energy, defined as the sum of products of the surface tension of interface ik , γ_{ik} , and the change in surface area of that interface $\Delta \sigma_{ik}$.

ΔA_B is the change in Helmholtz free energy due to body forces, in Equation 3 assumed to be limited to gravitational energy changes ($\sum m_l g \Delta h_l$, mass of element l , m_l times gravitational acceleration g times change in height Δh_l) and kinetic energy changes ($\sum m_n \Delta (v_n^2)$, mass m_n times change in (velocity squared), v_n^2).

Constancy of volume and temperature of each phase is assumed.

The surface tension, γ_{ik} , is defined according to Gibbs, recently reaffirmed by Johnson¹, as the specific (Helmholtz) surface free energy at constant temperature, volume and chemical composition, including modifications that have been made to the clean surface by adsorbed gases and vapours.

High energy surfaces, *i.e.* those with a high energy of formation for a clean surface (metals, inorganic crystals), will on all practical surfaces possess a surface tension determined largely by the adsorbed substances, including the vapour of the liquid studied. Low energy surfaces, *e.g.* organic substances, are less

influenced by the adsorption of vapour from the liquid, and their wetting properties are consequently much more reproducible, and more readily studied, for example, by the methods of Zisman *et al.*^{2, 3}

In the case of a drop of liquid approaching a perfectly smooth surface (Fig. 1),

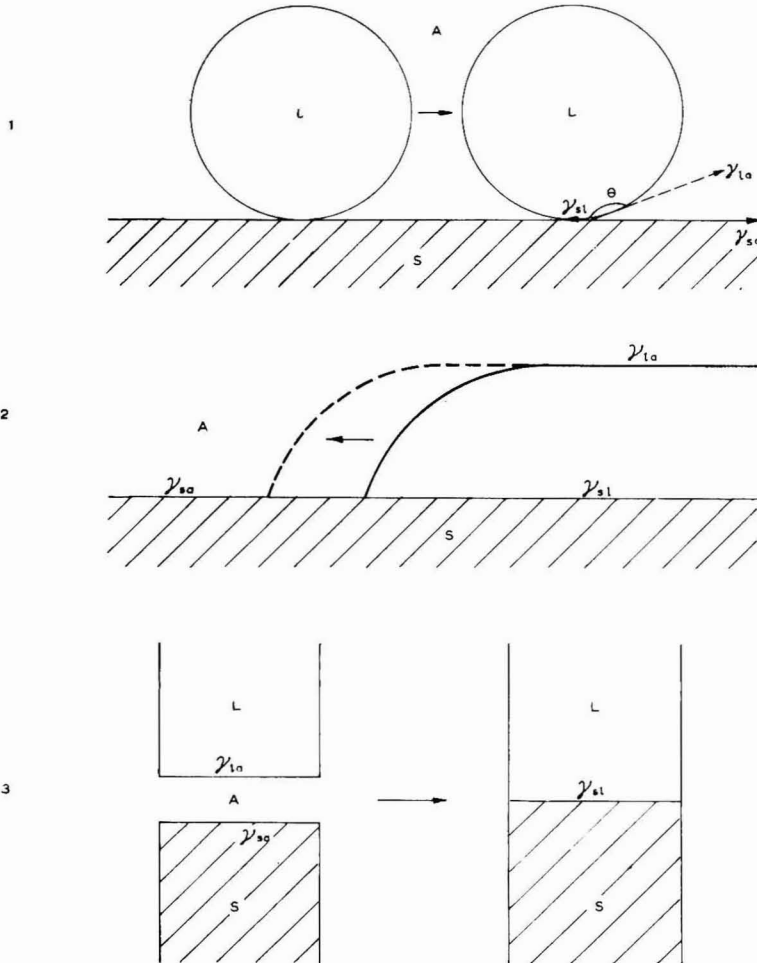


FIG. 1. ATTACHMENT OF A DROP OF LIQUID (L) TO A SMOOTH SOLID SURFACE (S)

FIG. 2. DERIVATION OF "SPREADING COEFFICIENT"

FIG. 3. DERIVATION OF "DUPRÉ'S EQUATION"

the first point to consider is the conditions under which the drop of liquid will attach itself to the surface. The condition for this is that there should be a decrease in free energy between positions before and after attachment. It has been shown^{1, 4, 5} that the surface energy and body force terms in Equation 1 must independently reach equilibrium; for the purpose of this argument it is therefore permissible to use Equation 2. For the case considered, three phases, liquid (l), solid (s), and air (a) are present and

$$\Delta \sigma_{sa} = -\Delta \sigma_{sl} \dots\dots\dots (4)$$

At the actual moment of attachment of the drop

$$\Delta \sigma_{la} = -\Delta \sigma_{sl} \dots\dots\dots (5)$$

where the condition for ΔA_s to be negative becomes

$$K = \gamma_{la} + \gamma_{sa} - \gamma_{sl} > 0 \dots\dots\dots (6)$$

$$\text{or } B = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} > -1 \dots\dots\dots (7)$$

The quantity K may be called the “attachment coefficient”, the sign of which determines whether the drop sticks or not. With smooth surfaces and most liquids in air it is always positive and this has led many people to forget its importance. It can be negative, however, with high surface tension liquids, such as liquid metals and molten salts, on ordinary smooth solids when there is non-attachment or complete non-wetting. The interchange of phases so that an air bubble approaches a smooth plane solid in a liquid may also give a negative value of K and consequently no attachment. Rough surfaces, and surfaces consisting of several surface phases (particularly entrapped air), can also give negative attachment coefficients which must be calculated in this case from Equation 2. The existence of such a negative coefficient is the condition for waterproofing, *e.g.* of textiles.

Conditions of Spreading

The conditions under which the drop of liquid attached to a smooth surface ($K > 0, B > -1$) will spread, will now be examined. The condition for complete spreading over the surface is that there is a surface free energy reduction in the final stages of spreading where the liquid/air interface is parallel to the solid (Fig. 2). Using Equation 2 again and substituting the condition (4) which still applies plus the condition

$$\Delta \sigma_{sl} = \Delta \sigma_{sa} \dots\dots\dots (8)$$

the condition for complete spreading becomes

$$S = \gamma_{sa} - \gamma_{la} - \gamma_{sl} > 0 \dots\dots\dots (9)$$

$$\text{or } B = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} > 1 \dots\dots\dots (10)$$

S is usually called the “Spreading Coefficient”, a term coined by Harkins^{6, 7}, who used it to study the spreading of liquids on liquids. It was, however, used earlier as a criterion for spreading on solids (“wetting power”) by Cooper and Nuttall^{8, 9}, who derived it from Quincke¹⁰. It should be noted that S is merely a criterion for spreading on a smooth surface and it is not, in general, equal to the free energy of spreading (which should be calculated from Equation 1), except for the special case of the spreading of a flat sheet of liquid parallel to the surface.

Finally, there is a region which satisfies the condition for attachment ($K > 0, B > -1$), but which does not satisfy the condition for complete spreading (*i.e.* $S > 0, B > 1$). In this region the drop attaches itself to the surface but does not spread completely, reaching an equilibrium condition in which the air/liquid

interface makes an angle θ , called the contact angle (Fig. 1), with the solid/liquid interface. The condition for this to occur is

$$-1 < B < 1 \dots\dots\dots (11)$$

and, under these circumstances only,

$$\frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} = B = \cos \theta \dots\dots\dots (12)$$

Equation 12 is called Young's Equation from its expression in words by Thomas Young¹¹. The validity of this equation has recently been considerably reinforced^{1, 4, 5}, but little mention has been made of the special conditions for its applicability laid down by Equation 11. These conditions can be described by the term "partial wetting".

The region where spreading is complete ($B > 1$) is referred to by Gans¹² as the region with "no contact angle", but this term could equally apply to the region where there is no attachment ($B < -1$); it is, therefore, probably best avoided. It is possible to have non-equilibrium contact angles in all of these regions.

Work of Adhesion

It is customary in a discussion of wetting and adhesion to introduce Dupré's equation¹³.

$$W_{sl} = \gamma_{sa} + \gamma_{la} - \gamma_{sl} \dots\dots\dots (13)$$

where W_{sl} is the work done, *i.e.* the decrease in Helmholtz free energy, when one flat square centimetre of liquid L is united with one flat smooth square centimetre of solid S in air A (Fig. 3). Equation 13 is, of course, a special case of Equation 2, in which the changes in interfacial area are defined in the special circumstances of Fig. 2.

W_{sl} is frequently termed the "Work of Adhesion". Dupré himself¹³ called it "force de réunion". Allowing for the confusion in those days between force and work, this is probably best translated as "work of union" (*i.e.* of two flat surfaces). It is clear that Dupré himself did not intend it to have a universal validity as a measure of adhesion. He did in fact state Equation 2 without the summation sign, and showed by his examples that he accepted the idea of multiplying area changes by surface tension to obtain changes in energy. Liquid applied to a solid surface is hardly ever in the contorted shape of Fig. 2 (although the application of an adhesive tape may be one example), and gravitational and kinetic energy changes have been ignored. The breaking of adhesive bonds may be governed to a considerable extent by electrostatic forces^{14, 15}, so that the reverse process to Fig. 2 does not usually obey Equation 13.

Most problems of wetting and adhesion involve interfacial area changes which are other than those assumed in Dupré's equation, and Equation 1 (which could, if desired, be termed the "Generalised Dupré equation") should be applied to the particular problem. The term "work of adhesion" for W_{sl} in Equation 13 is devoid of practical meaning and should be discontinued. In the particular case of a spreading drop in the absence of gravity, the application of Equation 2 involves a fairly simple numerical integration; with gravity present, however, it is a more difficult procedure. As Leja and Poling¹⁶ have recently pointed out, the term involving the area changes of the drop (bubble) is almost half the total surface energy change, so that Dupré's equation is quite inaccurate.

Effect of Surface Roughness

Few actual surfaces are ideally smooth, a condition which has been assumed up to now. Wood, the surface under consideration, is a typical surface which can never be completely smooth. The effect of roughness on the above equations can be simply derived from Equation 2. If by definition

$$\frac{\Delta \sigma_{ik}}{|\Delta \sigma_{ik}|} = f_{ik} \dots\dots\dots (14)$$

where $\Delta \sigma_{ik}$ is the actual area change of interface ik ,

$|\Delta \sigma_{ik}|$ is the apparent area, measured as a projection of the area $\Delta \sigma_{ik}$ on a plane parallel to the surface, and

f_{ik} is the roughness coefficient of the interface ik , assumed to be a constant, Equations 4—10, and 12 may be rewritten, replacing γ_{sa} by $f_{sa} \gamma_{sa}$, and γ_{sl} by $f_{sl} \gamma_{sl}$.

If it is assumed that $f_{as} = f_{sl} = f \dots\dots\dots (12)$

the modified equations become

$$K = \gamma_{la} + f (\gamma_{sa} - \gamma_{sl}) \dots\dots\dots (16)$$

$$S = f (\gamma_{sa} - \gamma_{sl}) - \gamma_{la} \dots\dots\dots (17)$$

$$B = \frac{f (\gamma_{sa} - \gamma_{sl})}{\gamma_{la}} \dots\dots\dots (18)$$

Equation 16 shows that sufficient roughening of a surface displaying partial attachment where $(\gamma_{sa} - \gamma_{sl})$ is negative (*i.e.* $B = \cos \theta$ is negative) will lead to non-attachment. This is the familiar principle that roughening a surface with a contact angle greater than 90° can secure waterproofing. Equation 17 shows that when $(\gamma_{sa} - \gamma_{sl})$ is positive (*i.e.* $B = \cos \theta$ is positive) roughening can convert partial wetting of a surface to complete wetting.

For the special condition where

$$-1 < \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} < 1 \dots\dots\dots (11)$$

and $-1 < f \frac{(\gamma_{sa} - \gamma_{sl})}{\gamma_{la}} < 1 \dots\dots\dots (19)$

$$\cos \theta' = f \cos \theta \dots\dots\dots (20)$$

where θ is the contact angle on a smooth surface of the solid and θ' is the apparent contact angle on the rough solid.

Equation 20 was first put forward by Wenzel¹⁷ and it has been shown to be thermodynamically correct a number of times^{18, 19, 20}. Only one study has established it experimentally, however, and that was for a system of two surface phases, metal and air (*i.e.* a metal gauze) by Cassie and Baxter²¹. The more extensive studies of Bartell and Shepard²² on artificially roughened paraffin wax were not explicable in terms of Equation 20. However, there is an assumption implicit in this equation which is not usually recognised. It is that f is a constant, identical in value for each surface profile adopted by the advancing liquid drop over the rough surface. There can be very few surfaces where this

is true. Even if the surface has the same value for f from one area to the next, it is probable that the profile taken up by the liquid/air interface advancing over (or receding from) the surface will pass through regions where the length of the profile divided by the length of a straight line joining its ends and parallel to the surface (F) will increase and decrease periodically. There will be maximum and minimum values of the "profile roughness coefficient". Wenzel's equation should then be written

$$\cos \theta = F \cos \theta' \dots\dots\dots (21)$$

where F is defined above. This provides an explanation for hysteresis of the contact angle which is not apparent from the usual way of expressing Wenzel's equation. An advancing liquid profile will tend to adopt a position where F is at its maximum value, while a receding profile will have a minimum value of F . Bartell and Shepard's results can be explained partly on this principle and partly by the fact that several phases were sometimes present on the solid (wax and air for some advancing liquids and wax and liquid for some receding ones). The examples of contact hysteresis caused by roughness given by Schwartz and Minor²³ are also explicable by the principle of varying values for F . Their illustrations, incidentally, make the point that F can vary with the angle made by the liquid/air interface with the surface and, indeed, there is no reason why the profile should be in one plane, in which case the measurement of F is rather difficult.

To conclude this section, it is believed that Wenzel's approach is quantitatively valid, though only when the concept of the roughness coefficient is based on a line profile instead of an area. It still lacks adequate experimental proof, however. The practice of improving adhesion by treating the surface with an abrasive has a double justification. It is liable to remove adsorbed films, thus increasing the value of γ_{sa} , and it increases the roughness coefficient F , giving higher values of S (Equation 16) or B (Equation 17).

Contact Hysteresis

In most practical examples where liquid comes into contact with a solid there is a difference between the wetting properties of the advancing liquid interface and those of the receding interface. These differences can cross over the boundaries between non-wetting, partial wetting, and complete wetting, but the receding interface is always displaced towards the direction of complete wetting by comparison with the advancing interface. Thus it is possible to have an advancing interface which does not wet a surface, but as soon as the system is made to move beyond the position of equilibrium by the operation of body forces (gravity, kinetic energy, etc.), partial wetting or even complete wetting can be obtained with a receding interface. Similarly, partial wetting on an advancing interface may be converted into complete wetting by the displacement of equilibrium.

There are three causes of contact hysteresis. More than one may be operating at the same time. The first is roughness; this has already been discussed in detail above and is due to the fact that the linear roughness coefficient usually passes through maximum and minimum values. The second is differences in adsorption on the advancing and receding surfaces. This may be expressed formally by a change in γ_{sa} before and after wetting, and to a lesser extent by a

change in γ_{sl} after prolonged contact with the liquid. The effect is particularly marked with high energy solids¹⁴. The third is a difference in the nature of the surface between advancing and receding conditions. An advancing liquid may entrap air bubbles which later dissolve or come to the surface of the liquid. There may be substances on the surface which dissolve in the liquid. Alternatively, a receding liquid may leave patches of liquid behind in grooves or it may deposit substances on the surface which were not there before.

The existence of contact hysteresis means that there is a difference between the surface energy change when a liquid spreads on a solid and the change in surface energy if the liquid is removed. Both these energy changes are of practical importance and, with a pure liquid, it can at least be said that the work of removal cannot be less than the work of application (N.B. for positive work, free energy change is negative). Unfortunately, with surface finishes even this generalisation cannot be made, because there is always a difference between the liquid which is applied to the surface and the final film, the adhesion of which is so important. The solvents which are lost in the process of film deposition leave a film with a different surface tension from that of the applied finish. The difference cannot be very great since resins can only be dissolved in liquids of similar polarity and, therefore, surface tensions. The polymerisation processes which occur in the hardening of drying oils or catalysed films also rarely account for an important change in surface tension. Important differences occur mainly when water or other hydroxylic solvents are present in the liquids. For example, aqueous urea-formaldehyde resins have a high surface tension before hardening, but develop a lower surface tension after hardening which can lead to difficulties of adhesion and even of spreading with the next layer. Latex coatings may similarly display a difference between the high surface tension of the aqueous suspension and the relatively lower value of the final film.

The Effect of Body Forces

It has already been mentioned that body forces, such as gravitational or kinetic energy, cannot influence surface equilibria; the above relations are, therefore, unaffected by body forces. In calculations of the free energy of wetting and spreading, however, they must be considered and Equation 1 must be used rather than Equation 2. The body forces also influence the equilibrium position of the whole system. Consequently, the equilibrium shape of a drop on a surface may be flattened by the action of a gravitational force towards the solid, so that both the liquid/air and liquid/solid interfaces have an increase in area. For partial wetting, gravitation can increase the actual wetted area of the solid at equilibrium (or reduce it if acting away from the solid), although it cannot influence the contact angle. In the absence of contact hysteresis, however, the wetted area will be reduced when the gravitational force is removed or reversed, e.g. by inverting the solid surface.

The permanent influence of gravitational or other body forces, such as kinetic energy (spray velocity, brush, knife, roller), is dependent on the existence of contact hysteresis. The body force can induce a greater area of solid to be spread by liquid, but without hysteresis the equilibrium area in the absence of the force will be assumed as soon as the body force is removed. Body forces are utilised in surface coating technology mainly to enable the operation of receding

interfacial conditions. As an example of a transition from no wetting to partial wetting the attachment of water to a proofed raincoat can be secured by heavy rain or by rubbing in the drops. The transition from partial to complete wetting happens with most surface coatings on solids and the whole function of body forces applied by spray, brush, roller, *etc.*, is to do this. Where this transition is not made, even if hysteresis takes place, the film will contract to its receding contact angle and “cissing” occurs.

Penetration into Porous Surfaces

Conditions for penetration into a porous surface are quite different from those for attachment and spreading on a flat surface. For a cylindrical open-ended capillary the condition for penetration to occur is

$$B = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} > 0 \dots\dots\dots (22)$$

which means that the contact angles must be below 90° or in the region of complete spreading. The advancing angle is what matters here, together with the size of the capillary, the viscosity of the liquid, the likelihood of gas pressure build up within the capillary and the change in viscosity of the liquid with time (*i.e.* drying time). A surface coating with a high initial and a lower final surface tension may show poor penetration and yet, if applied with sufficient energy to secure receding contact conditions (which should be those of complete wetting), displays adequate adhesion to the surface. This is typically found with latex coatings on wood or other porous surfaces, and with urea formaldehyde glue on wood in the manufacture of particle board.

The penetration of capillary spaces that are not cylindrical will differ somewhat from the simple picture just given. When complete wetting occurs there will be little modification, but if there is a finite contact angle there will be a chance of termination of penetration whenever a constriction in the capillary system is sufficient to reverse the curvature of the liquid/air interface²⁵.

The rate of penetration into an open ended cylindrical capillary, in the absence of gravitational or kinetic forces, is given by Washburn’s equation²⁶:

$$l^2 = \frac{\gamma_{la} \cos \theta}{2\eta} \frac{rt}{r} \dots\dots\dots (23)$$

where *l* is the distance travelled in time *t* into a capillary of radius *r* by a liquid with surface tension γ_{la} and viscosity η . θ is the contact angle:

$\gamma_{la} \cos \theta$ is frequently called the adhesion tension. It is only equal to $\gamma_{la}B$ within the region of partial wetting (Equation 11). With non-attachment the adhesion tension is $-\gamma_{la}$, and with complete spreading the adhesion tension equals γ_{la} .

Wood is one porous solid which does approximate to the conditions for applicability of Washburn’s equation whenever end grain surfaces are exposed, although the capillaries are not generally open ended. It should be noted that the amount of penetration to be expected is proportional to the square root of the period when the coating is liquid, to the square root of $\gamma_{la} \cos \theta$ and inversely proportional to the square root of the viscosity.

A rough surface can be regarded as a partially porous surface, since the depressions in the surface will behave in a similar way to a capillary in inducing concave curvature in the liquid/air interface and therefore promoting spreading.

The tendency of depressions and grooves to attract liquid into them (where the contact angle is below 90°) will, however, be balanced by the tendency of the protuberances to promote a convex liquid/air surface and consequently to delay spreading. Although the grooves will have tongues of liquid going into them, the bumps will have tongues of liquid in the other direction. This will have the effect, however, of considerably increasing the true roughness coefficient of the advancing liquid profile over that measured, for example, from a perpendicular section through the solid.

Non-Equilibrium Conditions

An actual spreading or wetting process does not occur at the infinitesimally slow rate necessary to ensure the establishment of equilibrium conditions. The equations and conditions that have been developed consist of criteria for wetting and spreading and means for calculating energy changes. During the process of reaching equilibrium, non-equilibrium wetting conditions can occur temporarily. Advancing interfaces display lower wetting characteristics than at equilibrium and receding interfaces higher wetting. A rapidly advancing interface may display non-wetting where there may be partial wetting at equilibrium. Complete wetting may be preceded by a finite temporary contact angle. Approach to equilibrium may be slow, particularly where adsorbed films are concerned. It may be very difficult to decide whether equilibrium has been reached or not, as there may be a slow long term change. This is particularly true of high energy solids, but it also applies to rough solids and porous solids. It is particularly difficult with the latter where there may be no definite equilibrium position at all. The final equilibrium established by a surface coating on a porous solid may be decided by the rate at which it sets. A non-hardening liquid might penetrate completely so that at equilibrium there is no surface film. In order to study the wetting and spreading behaviour of such a solid it is necessary to study pseudo equilibria, that is to say, the wetting behaviour of liquids spreading over the solid just fast enough so that they do not disappear into the solid. This approach is necessary with wood, for as Barkas²⁷ has pointed out, it is impossible to maintain a stable liquid interface on the surface for long periods. It is considered that the period of several seconds held in the experiments described below is very close to true equilibrium for a low energy surface such as wood, and an appropriate parameter for study of wetting behaviour.

Factors Influencing Spreading

In applying a surface coating to a surface the aim must be to achieve the maximum decrease of surface free energy during the spreading process. Again referring to Equation 1, this means,

- (a) a minimum value of γ_{la} , the surface tension of the liquid,
- (b) a minimum value of $\gamma_{sa} - \gamma_{sl}$ the difference between the solid surface tensions, and
- (c) a maximum value of $\frac{\Delta \sigma_{sl}}{\Delta \sigma_{la}}$ (the ratio of wetted solid area to loss of liquid/air interface).

Table I gives the values of surface tension for a number of typical clear wood coatings measured with a du Nouy Tensiometer, with results corrected by the

formula of Zuidema and Waters²⁸. As can be seen, most wood finishes, apart from the aqueous suspensions, have a low surface tension and it would hardly seem possible to reduce them further. It is rather remarkable that wood adhesives do not possess low surface tension values. Urea glues in particular have quite high values. Difficulties in their use are often associated with poor wetting.

TABLE I
SURFACE TENSION OF SOME WOOD FINISHES AND GLUES AT
20°C.

Finish	Surface tension (dyne/cm.)
Raw linseed oil	31.4
Medium oil phenolic varnish	23.7
Long oil phenolic varnish	25.9
Long oil alkyd varnish	25.6
Styrenated alkyd lacquer	25.1
Nitrocellulose lacquer	25.8
Alkyd/urea one can lacquer	26.0
Epoxy resin 2 can lacquer	28.0
Polyurethane 2 can lacquer	27.9
Polyvinyl acetate latex clear coating	38.6
Casein glue	46.6
Urea/formaldehyde glue	70.6
Phenol/resorcinol glue	47.7
Resorcinol glue	43.2
P.v.a. latex glue	38.5

When the condition of Equation 9 is satisfied, the difference $\gamma_{sa} - \gamma_{sl}$ can be obtained directly from a measurement of the contact angle by Young's Equation (Equation 10). However, many surface coating liquids, though not most glues, do not obey Equation 9 at an advancing interface (*i.e.* they spread spontaneously) and they cannot obey it on a receding interface otherwise cissing takes place. Measurement of $\gamma_{sa} - \gamma_{sl}$ on high energy surfaces is very difficult, since γ_{sa} will depend on the history of the surface and on atmospheric conditions to a considerable extent. It will also be influenced appreciably by adsorption of vapour from the particular liquid present, and this vapour may even act so as to prevent spreading of the liquid²⁹ ("autophobic liquids"). On low energy surfaces $\gamma_{sa} - \gamma_{sl}$ is fairly easily measured when partial wetting is present, from Young's Equation. Influence from atmospheric adsorption and from the liquid whose spreading behaviour is being studied is small and frequently negligible. In some cases it may even be possible to obtain values of γ_{sa} and γ_{sl} separately, from extrapolation of the surface behaviour of liquids of similar chemical composition to the solid. This was done by Fowkes and Sawyer³⁰ for fluorocarbons, and their work constitutes one of the few experimental proofs of Young's Equation. Kargin³¹ *et al.* does not consider that this sort of extrapolation is generally valid because of differences in molecular configuration between low and high molecular polymers.

The work of Zisman^{2, 3} and his collaborators has indicated a way in which the value of $\gamma_{sa} - \gamma_{sl}$ can be obtained for any low energy surface, even where

partial wetting conditions are not established, *i.e.* for non-wetting or complete wetting. They found that for many low energy solids there is a linear relationship between $\cos \theta$, *i.e.* $\frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}}$ and γ_{lc} of the form

$$\frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} = 1 + k (\gamma_c - \gamma_{lc}) \dots\dots\dots (24)$$

where γ_c is known as the critical surface tension for spreading,
 k is the slope of the line, and
 θ is the contact angle, which on most of Zisman's surfaces displayed no hysteresis.

On a rough surface this becomes

$$F \frac{(\gamma_{sa} - \gamma_{sl})}{\gamma_{la}} = 1 + k (\gamma_c - \gamma_{lc}) \dots\dots\dots (24a)$$

where F is the profile roughness coefficient, maximum values being taken for advancing angles and minimum values for receding angles.

The concept of critical surface tensions has recently been applied as a guide to surface coating behaviour on metal surfaces³². It was confined to receding interfaces, however, and failed to take full notice of the inevitable difficulties of high energy surfaces. James³³ also showed how contact angle measurements could give a guide to adhesion of surface coatings on metal surfaces. Equation 24 can be used to determine $\gamma_{sa} - \gamma_{sl}$ in regions of non-spreading or complete spreading, from measurements made in the region of partial wetting. Similar liquids should be used since the differences in γ_{sl} caused by different chemical substituents may lead to several different straight lines, even with hydrocarbon surfaces³⁴.

Having determined $F (\gamma_{sa} - \gamma_{sl})$, the energy change in any particular case of spreading or wetting can be calculated from Equation 1, provided that the difference between F and f , the mean roughness coefficient, is small or known. As a comparison between different liquids or on different surfaces, it is useful to define a standard situation. The simplest is the energy change when a spreading liquid with a large area parallel to the solid covers an extra projected square centimetre of solid (Fig. 3). The energy change in the special case is given by the spreading coefficient S .

$$S = f (\gamma_{sa} - \gamma_{ls}) - \gamma_{la} \dots\dots\dots (17)$$

and the value of S is a convenient measure of the energy with which any particular liquid will attach itself to a particular surface.

SPREADING OF LIQUIDS ON WOOD

Wood may be considered as a low energy solid so that study of its wetting properties is easier than that of metals. Its surface properties do not change violently with age or preparation. It does present special difficulties, however, and consideration of these should assist in the extension of work on wetting properties of solids from flat surfaces of known chemical composition, to rough or porous materials of uncertain composition which so frequently have to be dealt with in practice.

The chemical composition of wood is only imperfectly understood. It consists mainly of cellulose (32-62 per cent), lignin (17-40 per cent), hemicelluloses, starches, pectins and sugars, with small quantities of tannins, colouring matters, resins, inorganic salts, *etc.* The actual amounts of these constituents vary from tree to tree and with the method of estimation, and the categories overlap so that for any particular analysis, summing the totals of the constituents gives well over 100 per cent. Even the most important and best understood of these constituents, cellulose, may not be so simple as was once believed³⁵. Lignin, despite much concentrated attack, has still to be given an unambiguous chemical formula, and the minor constituents, though many definite chemical compounds have been isolated, have yet to be exhaustively identified for any single piece of wood. Some of these minor constituents, particularly the resins, fats and volatile oils, can have a major effect on surface properties. Changes in the nature and amounts particularly of minor constituents take place continually with ageing. On top of the chemical complexity of the wood itself is the overriding importance of moisture content. Wood absorbs or loses moisture with any change in the humidity of the surrounding atmosphere. The surface properties are changed, as well as the dimensions of the specimen, to a different extent in the three main directions of the tree (tangential, radial and longitudinal). Loss and gain of moisture takes place along different paths, causing hysteresis. Difficulties with water vapour also affect the measurement of wetting properties on high energy solids³⁶. Finally, wood is anisotropic. Most of its properties are different in the three different directions in the tree, and its surface properties are no exception. It is probable that differences in surface profile are responsible for these wetting differences, but it is by no means certain that there may be some kind of chemical anisotropy involved since anisotropy in wood does extend to the molecular level, as has been shown by electron micrographs.

While no systematic study has been made of wetting behaviour on wood, it is recognised to be a property which must be related to the performance of surface coatings and glues. Freeman³⁷ and Freeman and Wangaard³⁸ have been able to relate glue bond quality in wood to its wettability, as measured by contact angles, although the relationship was statistical and not based on any theoretical analysis. Suzuki³⁹ related contact angle and "tumbling angle" on silicone treated wood to its roughness. Allan⁴⁰ found a correlation between the spreading and adhesion of printing inks on polyethylene and the contact angle of water droplets. Allan and Roberts⁴¹ made a rather qualitative study of the effect of roughness on wettability of perfluorocarbon films. These are two typical low energy surfaces, the behaviour of which might have some bearing on the surface treatment of wood, another low energy surface.

Rather more relevant are the few studies on cellulose. Ray, Anderson and Scholz⁴², in a study on cellulose derivatives, did a limited number of measurements (three, in fact) on viscose cellulose and got a critical surface tension for spreading of 44 dyne/cm. They showed that various native celluloses before extraction could depart greatly from this value, because of surface active materials present on the surface. Orchon⁴³ and Ekwall and Andresen⁴⁴ have both applied the method of contact angle determination to the study of adhesives and other liquids on paper, which differs from wood in having part of its constituents removed and being made almost isotropic in the horizontal plane.

Finally, Borgin⁴⁵ has made a fairly thorough study of the wetting behaviour of cellulose films. He is one of few investigators who gives the accuracy of contact angle measurements, and he demonstrated that the wettability of cellulose increases with the moisture content.

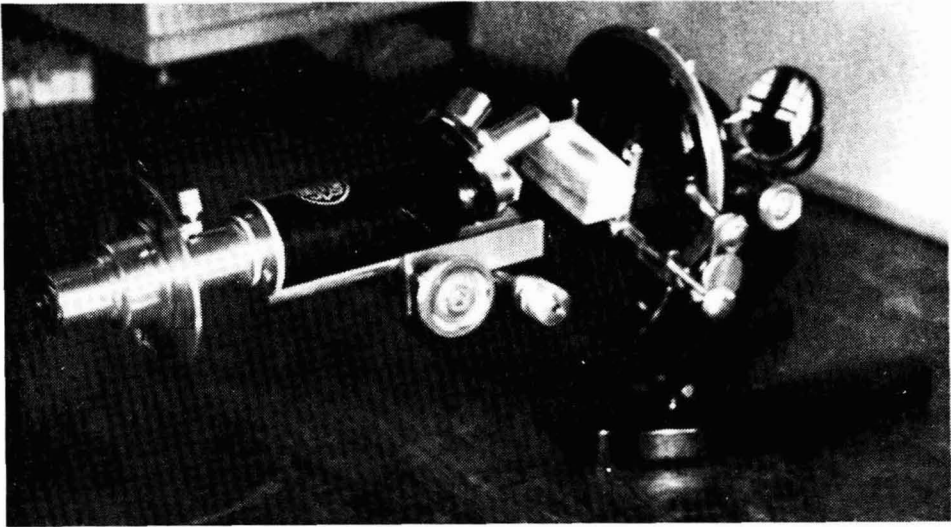


FIG. 4. APPARATUS FOR THE MEASUREMENT OF CONTACT ANGLE ON WOOD

Experimental Study of Wetting on Wood

Contact angle measurements on wood were made by the horizontal microscope technique. A microscope with a goniometer eyepiece and a rotating stage was in its horizontal position (Fig. 4). Wood specimens were held in the stage by a rubber band. Liquids were placed on the surface by means of a syringe. The stage was rotated until the drop began to advance, then moved back until it was just stationary, and the angle of contact measured by the goniometer eyepiece. In this way several measurements on different parts of the sample could be made with the same liquid drop, even when it penetrated the wood. However, results were ignored when the penetration of the liquid was so rapid that it spread in advance of the drop. Wood samples were prepared in such a way that the three grain directions of the wood could be studied. Thirty measurements were made with each surface and each liquid. The mean of $\cos\theta$, the standard deviation and the 95 per cent confidence limits were calculated by standard methods.

Most of the work was done on freshly planed surfaces. Some experiments were also performed on sawn surfaces, but only in a few cases was the reproducibility, or freedom from uncontrolled spreading, sufficient for measurement to be possible. The selection of species for study was made so as to be fairly representative, but also to avoid the most obvious experimental difficulties associated with coarse-grained and resinous woods. The species chosen were as follows:

Beech, *Fagus sylvatica*, the most common furniture hardwood. It has a uniform texture but is rather permeable to liquids.

Greenheart, *Ocotea rodiaei*, a heavy uniform grain hardwood which has a reputation for difficulty in finishing and gluing.

Western hemlock, *Tsuga heterophylla*, a fairly common softwood containing little resin but possessing prominent growth rings.

Parana pine, *Araucaria angustifolia*, a South American softwood with a very uniform texture used for joinery.

The liquids used for contact angle measurements are given in the table below.

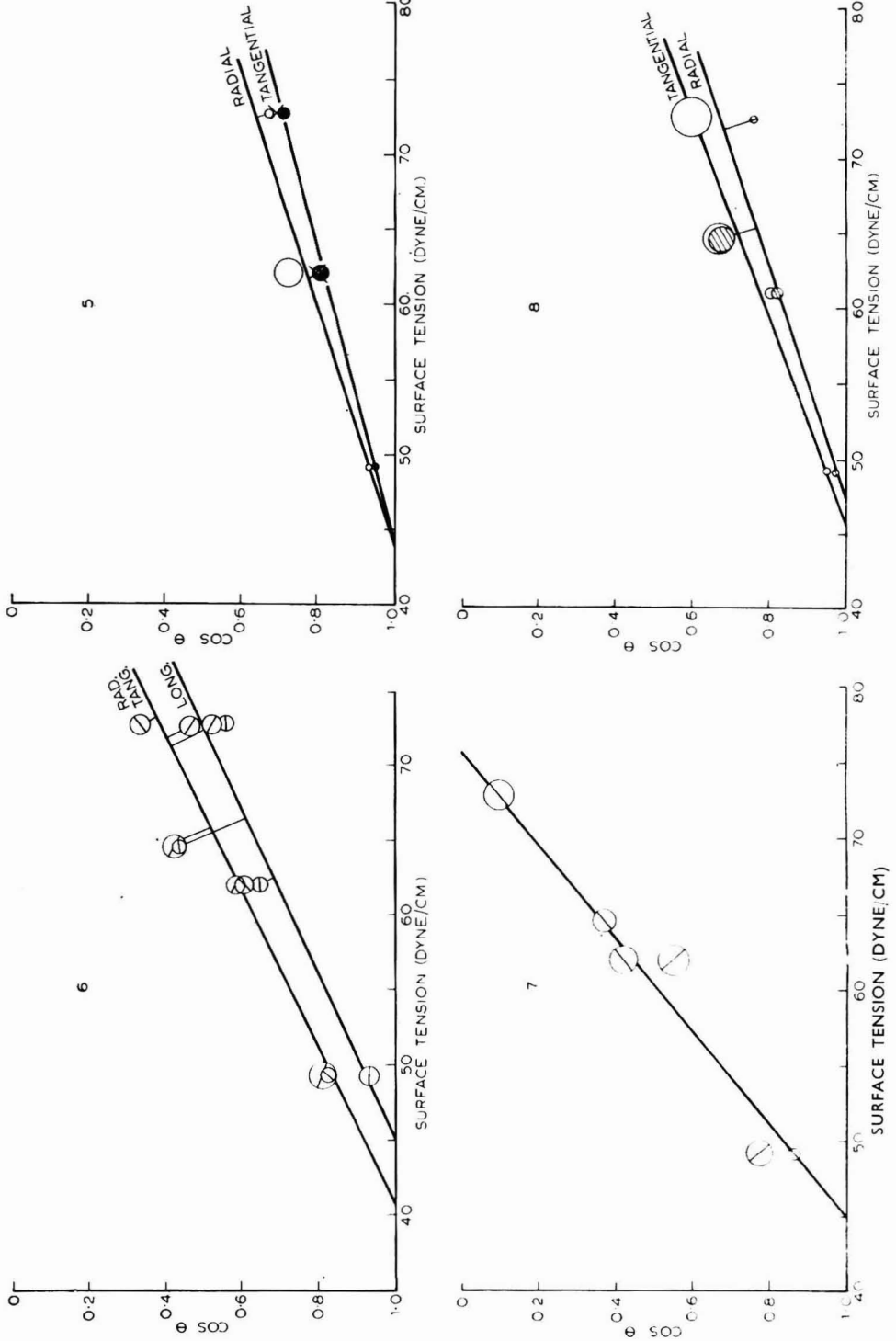
Liquid	Surface tension (dyne/cm.)*
Distilled water ..	72.8
Glycerol	62.8
Ethylene glycol ..	47.7

*All at 20°C

In the early measurements it was noticed that glycerol sometimes gave rather anomalous results. This is probably due to its high viscosity, which causes the entrapping of air, similar to the observations of Bartell and Shepard²². A dilute solution of acetic acid (surface tension 61.6 dyne/cm.) was therefore also used, as representative of a liquid of similar viscosity to water. Some representative plots of $\cos \theta$ against surface tension are shown in Figs. 5-8. The size of the spot indicates the 95 per cent confidence limits. From these graphs values can be obtained for the critical surface tension γ_c and k , the slope of the line through the points in Equation 24a; values of γ_c and k are given in Table II.

TABLE II
VALUES FOR γ_c AND k FOR ADVANCING LIQUIDS ON TIMBER SURFACES

Timber species	Face	Direction	γ_c dyne/cm.	k cm./dyne
Parana pine (planed)	TL	Tangential	45.0	0.0142
	TL	Longitudinal	56.0	0.0132
	RL	Radial	45.3	0.0115
Western hemlock (planed) ..			38.2	0.0102
Beech (planed)			42.8	0.0096
Greenheart (planed)	TL	Tangential	43.7	0.0294
	TL	Longitudinal	45.3	0.0205
	RL	Radial	43.5	0.0267
	RL	Longitudinal	45.2	0.0200
Greenheart (sawn)	TL	Tangential	42.0	0.0290
	TL	Longitudinal	44.5	0.0251
	RL	Radial	43.9	0.0317
	RL	Longitudinal	42.9	0.0257



Cos θ PLOTTED AGAINST SURFACE TENSION FOR BEECH, PLANED (FIG. 5), GREENHART, PLANED (FIG. 6), GREENHART, SAWN (FIG. 7), AND PARANA PINE, PLANED (FIG. 8).

The table shows that the critical surface tension for spreading is usually 42-45 dyne/cm. This is similar to the values obtained for smooth cellulose (44 dyne/cm.) by Ray, Anderson and Scholz⁴², whose value for k (0.033) was rather higher than most of the values in Table II, except those for sawn greenheart. From Table I it can be seen that all wood finishes spread spontaneously on wood, while glues are either on the borderline of spreading or are in the region of partial wetting only. This table also shows a surprising similarity, both in critical surface tension of spreading and k values, for the three directions in the wood. It is a matter of common experience that liquids appear to wet wood most readily in the direction of the grain. These results show what is evident from closer inspection, that the reason for this is not the greater ease of wetting, but the greater ease of penetration by liquids of wood in the grain direction. This may cause wetting of the surface from beneath, which helps spreading. The difference between species seems to lie more in the values of k than in γ_c . Greenheart, for instance, which has the reputation of being difficult to glue, has a lower wettability by liquids with high surface tensions, but with low surface tension liquids it is actually more easily wettable than the other species. The results on sawn greenheart show that k increases with increased roughness, as would be expected from Equation 24a.

It is possible from Equation (24a) to obtain values for $B = F(\gamma_{sa} - \gamma_{sl})/\gamma_{la}$, and if F for an advancing interface is assumed to be equal to f , the average roughness coefficient of the surface, the spreading coefficient S can be derived from Equation 17. These quantities are tabulated in Table III for four wood

TABLE III
SPREADING PROPERTIES OF SOME SURFACE COATINGS ON VARIOUS TIMBERS

Timber species	Liquid	B	Spreading Coefficient S dyne/cm.
Parana pine (planed)	Phenolic varnish	1.28	6.5
	Polyurethane lacquer	1.25	7.1
	P.v.a. latex	1.08	3.3
	Urea-formaldehyde glue	0.67	-23.0
Western hemlock (planed)	Phenolic varnish	1.15	3.5
	Polyurethane lacquer	1.10	2.9
	P.v.a. latex	1.00	-0.2
	Urea-formaldehyde glue	0.67	-23.3
Beech (planed)	Phenolic varnish	1.18	4.3
	Polyurethane lacquer	1.14	4.0
	P.v.a. latex	1.04	1.6
	Urea-formaldehyde glue	0.73	-18.9
Greenheart (planed)	Phenolic varnish	1.50	11.8
	Polyurethane lacquer	1.40	11.1
	P.v.a. latex	1.14	5.4
	Urea-formaldehyde glue	0.37	-44.6
Greenheart (sawn)	Phenolic varnish	1.55	13.0
	Polyurethane lacquer	1.43	12.0
	P.v.a. latex	1.13	5.1
	Urea-formaldehyde glue	0.13	-61.6

finishes; medium oil phenolic varnish ($\gamma_{la}=23.7$ dyne/cm.), 2 can polyurethane lacquer ($\gamma_{la}=27.9$ dyne/cm.), polyvinyl acetate latex coating ($\gamma_{la}=38.6$ dyne/cm.), and urea/formaldehyde glue ($\gamma_{la}=70.6$ dyne/cm.). For calculation of these figures averages of γ_c and k for the three directions on the wood have been taken.

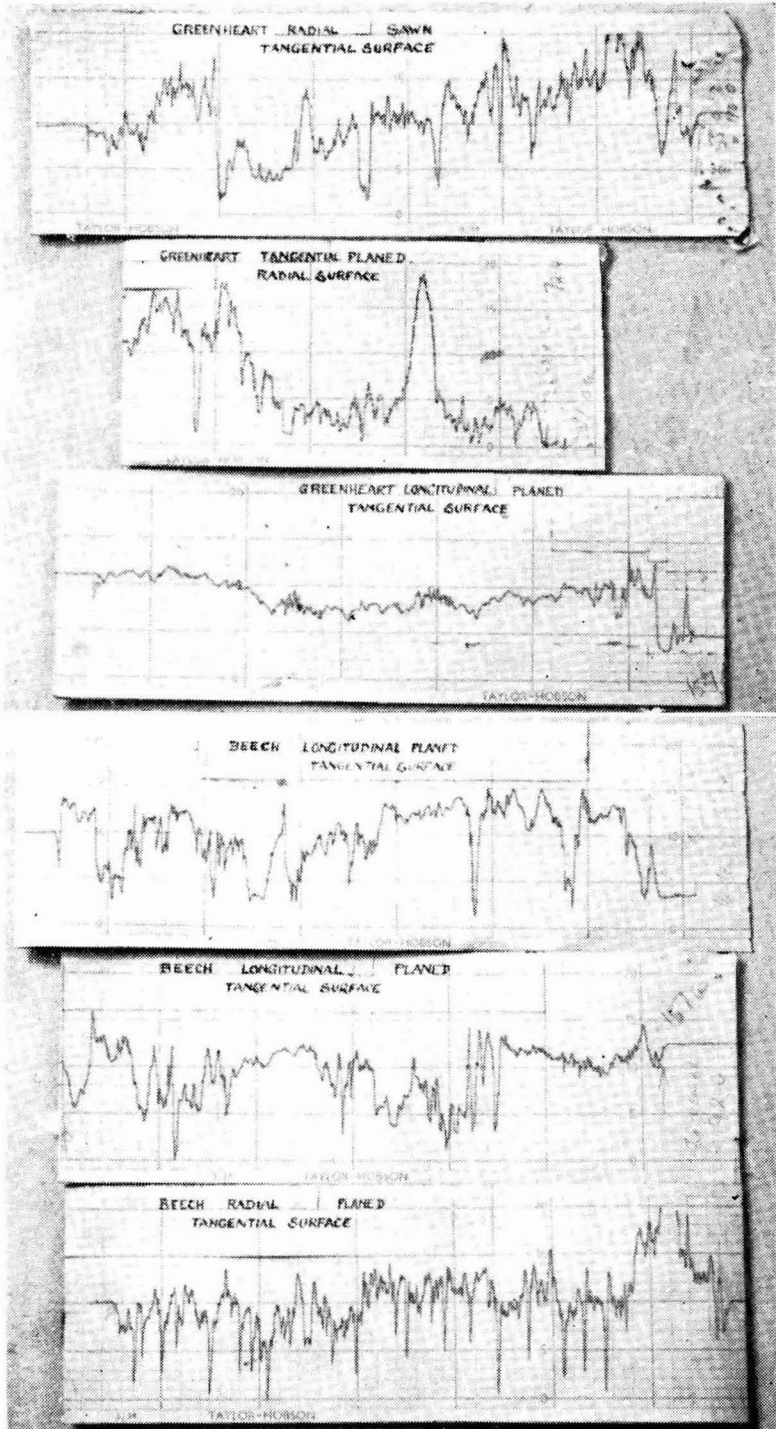
Roughness Coefficient

The measurements so far have been obtained without an actual determination of the area roughness coefficient f or the profile roughness coefficient F . The similarity of γ_c to the value obtained with smooth cellulose indicates that the value of f is small. The assumption made in calculating the spreading coefficient is that the maximum value for F is not very different from its mean value. Actual measurements of roughness coefficients on surfaces such as wood are beset with difficulties. An attempt was made to use the profile measurements obtainable with the *Talysurf* instrument. Some profiles obtained with this instrument, which provides a magnified trace of the movement of a sapphire stylus over the surface are given in Figs. 9-11. The horizontal scale is magnified twenty times and the vertical scale 1,000 times. From these traces profile roughness coefficients F can be calculated by measuring vertical movements, with a map measurer; roughness coefficients thus obtained are given in Table IV.

TABLE IV
MEAN PROFILE ROUGHNESS COEFFICIENTS FOR WOOD SURFACES ACCORDING TO *Talysurf*
INSTRUMENT
T=tangential R=radial L=longitudinal

Timber species	Face	Direction	Roughness Coefficient, f
Parana pine (planed)	TL	T	1.015
		L	1.0033
Western hemlock (planed)	RL	R	1.024
		T	1.011
Beech (planed)	TL	T	1.018
		L	1.0074
Greenheart (planed)	RL	R	1.014
		T	1.018
Greenheart (sawn)	TL	L	1.0102
		R	1.0074
	RL	T	1.013
		R	1.014

It will be noted that the values for f are surprisingly low, only influencing values of $\cos \theta$, for instance, by one to two per cent, generally within experimental error. There are several reasons for believing that these values are too low. The instrument is designed to measure roughness of polished metal surfaces and the profiles obtained were, even with the lowest magnification available, from specially smooth areas of wood, otherwise it was difficult to keep the recorder on the scale. The stylus itself tends to smooth out the actual rough surface so that the actual profile is longer than the recorded one. Then, as has



ROUGHNESS PROFILES (VERTICAL MAGNIFICATION $\times 1,000$, HORIZONTAL MAGNIFICATION $\times 20$)
FIG. 9 (Upper) GREENHEART. FIG. 10 (Lower) BEECH

been pointed out, actual liquid profiles may have tongues of liquid going into grooves and retarded areas on bumps, besides being at an angle to the surface, the profile being longer than a perpendicular section. Despite this it is doubtful whether the true roughness values could be higher than 1.05 or 1.10. This is quite insufficient to explain the contact hysteresis displayed by all the liquids on wood, which must therefore be caused by adsorption and surface phase composition differences. Such small values of F are unlikely to mean that there can be much error in assuming that the maximum values of F are close to mean values, so the figures for S should be reasonably accurate.

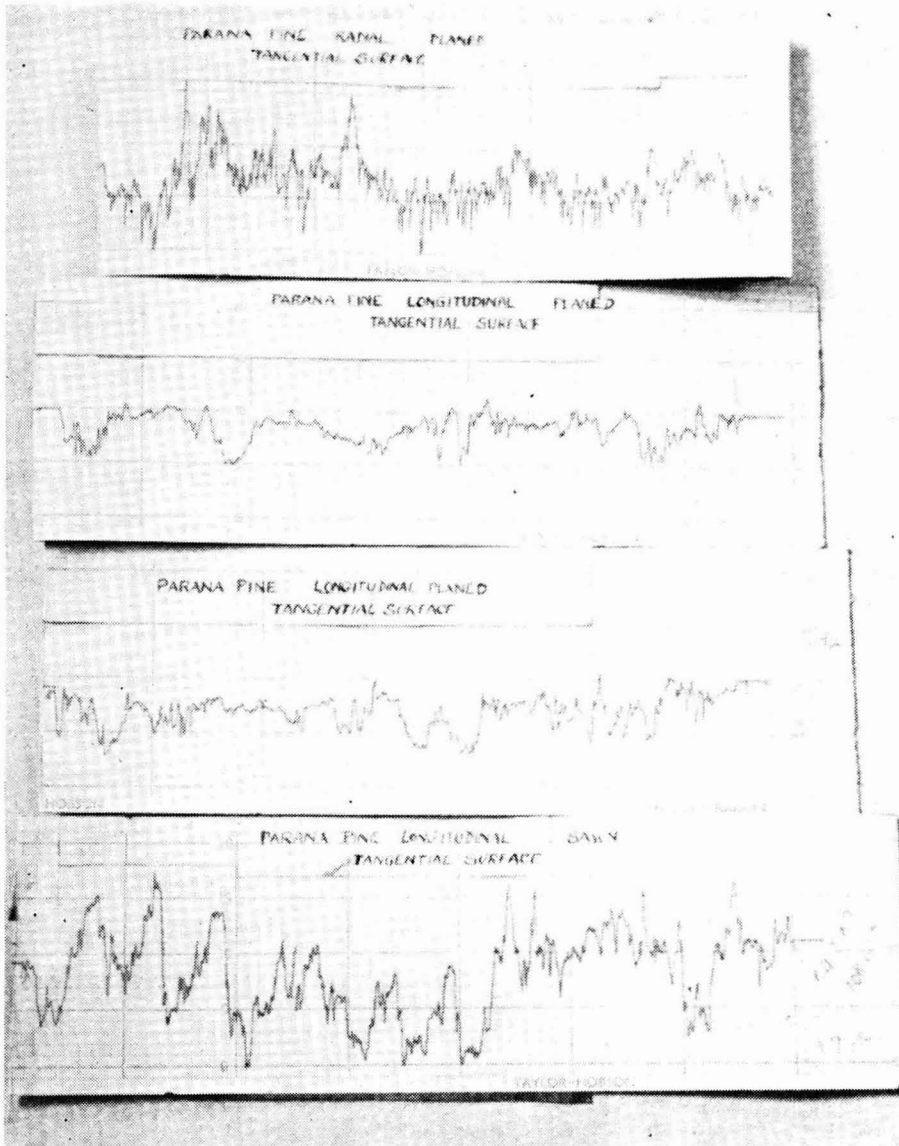


FIG. 11 ROUGHNESS PROFILES (VERTICAL MAGNIFICATION $\times 1,000$, HORIZONTAL MAGNIFICATION $\times 20$)—PARANA PINE

THE ADHESION OF SURFACE COATINGS TO WOOD

The preceding argument has been devoted to the calculation of the energy change taking place when a surface coating liquid is applied to a wood surface. This has a direct bearing on the ease of carrying out the coating operation, but it is less directly related to a very vital property of the coating in use, *i.e.* the ease with which the coating can be removed. There are many drawbacks to the accurate measurement of this property. The surface coating industry employs a range of empirical tests for adhesion without much attention being paid to the forces involved. Even when forces are measured, unexpected difficulties arise. Failure may occur in the coating or in the substrate and not at the interface between the two. Stress concentration due to swelling or shrinking may build up in both the coating and the substrate. Actual stresses applied during testing may be very difficult to determine. If a test is carried out at a measurable speed, electrostatic forces may be more powerful than the thermodynamic forces^{14, 15}. A review of these difficulties has recently been given by De Bruyne¹⁶. This paper will give a few relevant examples from the field of surface coatings on wood.

Adhesion caused by surface coatings is an important problem in the development in the use of floor seals. When applied to a new wood block floor the seal tends to stick the blocks together so that if shrinkage of the floor occurs in response to a fall in humidity unsightly gaps may appear in a few places instead

TABLE V
CLEAVAGE STRENGTH OF 2 CM. SQUARE BEECH JOINTS STUCK WITH FLOOR SEALS

Seal	Wood surface	Mean breaking strength (lb.)	Mean wood failure (%)	No. of Specimens
Shellac	Planed	8	0	1
	Fine sawn	51	0	3
Oleoresinous I	Planed	28	0	3
	Fine sawn	29	0	3
Oleoresinous II	Planed	16	0	6
	Fine sawn	22	0	6
<i>Epikote</i> ester	Planed	48	0	1
	Fine sawn	43	0	3
One can U-F I	Planed	77	30	3
	Fine sawn	69	19	6
One can U-F II	Planed	50	10	6
	Fine sawn	54	2	6
2 can U-F I	Planed	45	1	3
	Fine sawn	72	45	3
2 can U-F II	Planed	29	0	3
	Fine sawn	59	16	3
2 can U-F III	Planed	98	73	3
	Fine sawn	109	26	3
2 can U-F IV	Planed	68	1	3
	Fine sawn	79	22	3
2 can Epoxy	Planed	77	32	3
	Fine sawn	100	37	3
2 can Polyurethane	Planed	50	0	1
	Fine sawn	80	71	3
p.v.a. Primer	Planed	15	0	2

of unnoticed small gaps all over the floor. The relative importance of this effect may be determined by an adhesion test. The test chosen was performed on standard cleavage test pieces of beech, similar to those employed for testing the cleavage strength of wood⁴⁷, except that these were in two halves, stuck together with the surface coating material. One coat was allowed to dry on each surface and a second coat was applied, dried until tacky and then the two halves clamped together and held for one month before testing; the results are given in Table V.

These results are a useful guide to the likelihood of the seal sticking together wood blocks. The results require interpretation with some caution, however. Those finishes which give an appreciable proportion of wood failure are the most undesirable, since movement of the floor may lead to splitting of the wood. The strength values in these cases represent behaviour of the wood. The oleoresinous finishes, shellac, and p.v.a. primer give fairly low strength values and no wood failure; they are, therefore, to be preferred where absence of adhesion is important. Failure in all these cases was in the finish itself, which is indicative of its lack of strength and consequently of its abrasion resistance as a floor surface. The most resistant finishes are thus the strongest adhesives. The adhesion problem is best overcome by a priming coat with weak adhesion such as shellac, p.v.a., oleoresinous or wax (the latter must be removed by sanding before applying further coats), followed by an abrasion resistant surface. This problem is hardly at all connected with the attachment of the finish to the wood.

Another important problem of clear coatings on wood is their resistance to exterior weathering. The development of timber for exterior use on buildings is seriously hampered by the absence of a satisfactory durable clear coating, the maximum maintenance period for four coats being at present about three years⁴⁸. The typical mode of failure displayed by the best of these finishes is shown in Fig. 12. This failure is an adhesion failure and the approach taken by many manufacturers to improve durability of coatings is to improve the adhesion of the coating, particularly by improving the penetration of the primer coat by dilution or by use of a special adherent primer. Some experiments were done in which comparative tests were made on the durability of a long oil alkyd resin varnish on oak and Western red cedar panels which had been pretreated with a number of chemical "keying agents" or adhesion promoters. These included vinyl chlorosilane and other silicones, stearatochromyl chloride, t-dodecyl mercaptan, butyl titanate, fatty amines, and a number of long chain wetting agents. The durability of the long oil alkyd film was in all cases reduced.

This reduction in durability can only be explained if adhesion is already adequate. Close examination of Fig. 12 shows that grain marks from the wood are on the underside of the detached film, and if a piece of detached film is examined under the microscope (Fig. 13), it may be seen that there is a considerable amount of wood fibre still attached to the film. The failure of adhesion has occurred in the wood surface itself. The mechanism of failure is that the film under the combined action of sun (evaporation, degradation and cross-linking) and rain (leaching out of low polymers and plasticisers, hydrolysis), becomes brittle and eventually cracks over a weak point. Water then enters beneath the film, spreads at the interface and hydrolyses the surface



FIG. 12. TYPICAL VARNISH FAILURE ON WOOD AFTER WEATHERING

FIG. 13. UNDERSIDE OF DETACHED VARNISH FILM AFTER FAILURE ON A HARDWOOD (MORA) (MAGNIFICATION $\times 66$)

FIG. 14. PREMATURE BREAKDOWN OF VARNISH FILM BY RESIN EXUDING FROM DUCTS (KAPUR) (MAGNIFICATION $\times 66$)

wood fibres so that in the next swelling cycle of the film caused by rain it begins to peel off. It follows that increased durability is not to be expected from improvements in adhesion but in film stabilisation. Experiments have confirmed that dilution of the first coat of varnish to give better penetration is normally unnecessary and greater durability is given from the thicker film, when the first coat is not diluted. The incorporation of ultra-violet absorbers in the film can increase its life, however, by as much as six months.

The factors controlling durability of surface films on wood are, therefore:

- (a) The adhesion of the film to the substrate, which should be fairly closely related to the calculations of spreading coefficient in Table III.
- (b) The resistance of the film to weathering, particularly to leaching and chemical changes, causing embrittlement.
- (c) The swelling properties of the film in water and its permeability to water vapour.

The first property, adhesion of film to substrate, seems to be a great deal more satisfactory than many people realise. A number of timbers display "poor adhesion" because they contain resins and oils. Such timbers include teak, pitch pine and many members of the South East Asian genus *Dipterocarpaceae*, such as keruing, gurjun, meranti and kapur. Rather limited experiments which have been carried out have indicated that film stability on teak and resinous pitch pine is not reduced by the resin present, provided that a short oil primer which is not permeable to the resin is used. In the absence of such a primer the resin exudes from its ducts in the wood and softens the film above it (it contains powerful solvents). The film becomes sticky, holds dirt particles, and these enable water penetration through the film, initiating premature breakdown; this is shown in Fig. 14. If an impermeable film is used, as much as possible must be done to enable relief of resin pressure by leaving the backs of panels, *etc.*, unpainted.

As has been stated above, adhesion to the wood should be improved on rough surfaces and this is doubtless the explanation for the greater durability of paint films on sawn wood surfaces found by Andersson and Nylen⁴⁹. There are other factors to be considered, however. The roughened surface doubtless provides a reinforcement for the first paint layer. If it is too rough it could even provide a weakened surface and lowered adhesion. Suchsland⁵⁰ found that glue joint strengths in wood reached a maximum with increasing roughness, after which they fell, due to weakening of the surface layers.

The weather resistance of surface films, needs little comment, except that the inability of the modern plastics industry to produce a really weather resistant plastic is one of its greatest and least publicised failures. The requirements are, of course, rather stringent, since chemical stability in a very thin film is difficult to achieve. It is, however, a little surprising that of the innumerable synthetic polymers that have been produced since the heavy organic chemical industries got into their stride, only a few approach the exterior durability of long established drying oil varnishes and there are none which exceed the durability of the earliest modifications introduced by the plastics industry when phenolic and alkyd resins replaced natural resins in oil varnishes. This failure can be traced to three causes, First, the inability to control molecular weight distribution. Low polymers which volatilise or leach out are almost always present, and when

they go flexibility is lost. Secondly, the lack of understanding of degradation mechanisms. Thirdly, the exclusive concentration on carbon compounds. There is a chance that really stable films might be obtainable from polymers based on the geologically stable elements such as silicon, phosphorus and aluminium. Certainly a surface coating which possessed the weathering qualities of glass would solve all conceivable requirements. The importance of the behaviour of surface films towards water is frequently underestimated and, indeed, the unsatisfactory properties of many such films represents a fourth challenge to the polymer chemist.

Most surface coating films swell appreciably in water and the cyclic stresses applied to the surface layer of the wood by alternate periods of rain and sun undoubtedly play a major part in its ultimate detachment. Browne⁵¹ has particularly stressed this point with the conventional paints and their vehicles, but it is doubtful whether any of the recently developed resinous coatings possess greatly superior resistance to water. Permeability of the film to water vapour is related to its ability to swell in water. It acts in a rather complex fashion. In certain circumstances a film which is resistant to water vapour actually loses adhesion to the wood because of this fact. Wood which is heated in the sun invariably loses water vapour, particularly if it was damp when painted, or if it has been subjected to a winter temperature gradient with the cool outer surface film acting as a condenser for the humid air diffusing through the wood structure. If the water vapour produced by sunshine cannot pass easily through the surface film very high pressures can build up and cause the familiar blistering. Such blistering is enhanced by dark colours and by moisture resistant alkyd and phenolic media. It is particularly noticeable with woods with a coarse structure, such as oak, where water tends to evaporate selectively from the large vessels.

The surface coating that is most resistant to water vapour is aluminium primer. Resistance to water vapour can be a very valuable property and aluminium primer is particularly recommended for treatment of end grain surfaces of wood and for really dry wood. It should not be used on damp wood and if employed in house painting it should be used on interior woodwork as well as exterior. Indeed its use on the interior surfaces of woodwork should eliminate all cases of exterior paint blistering which is a difficulty encountered with increasing frequency today.

PENETRATION OF SURFACE COATINGS INTO TIMBER

Penetration is usually regarded as one of the essential properties of any surface coating on wood. It is supposed to "feed the wood", "provide a key" and "reinforce the fibres". It is now generally accepted that penetration and "providing a key" is not necessary with a wood adhesive. Browne and Truax⁵² showed that a low melting metal alloy which does not wet the wood has no adhesive properties even if penetration occurs. Penetration may actually reduce the effectiveness of an adhesive, since it tends to produce a starved joint. This is probably one reason why wood adhesives do not have maximum spreading properties (Table I).

The penetration of glue into timber does not resemble the conventional concept of a key half turned in a lock or a tooth filling. Penetration is preferentially

along end grain fibres which behave as closed cylindrical capillaries. The amount of penetration depends on the angle made by a particular surface with the grain of the wood. Suchsland⁵³ has shown that penetration does increase the strength

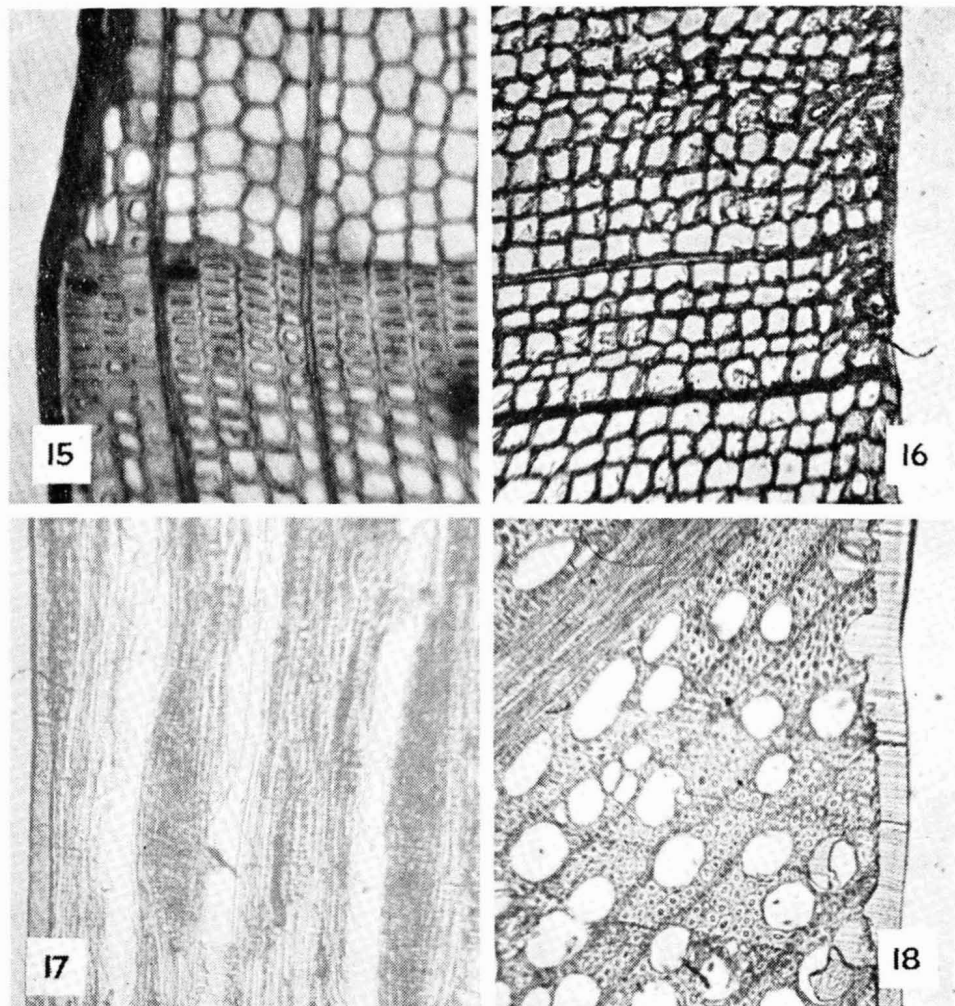


FIG. 15. TRANSVERSE SECTION OF RADIAL SURFACE OF WESTERN RED CEDAR TREATED WITH TWO COATS OF A LOW VISCOSITY "PENETRATING" OLEORESINOUS FLOOR SEAL. (MAGNIFICATION $\times 420$).

FIG. 16. TRANSVERSE SECTION OF TANGENTIAL SURFACE OF WESTERN RED CEDAR TREATED WITH TWO COATS OF A HIGH VISCOSITY OLEORESINOUS FLOOR SEAL. (MAGNIFICATION $\times 420$)

FIG. 17. LONGITUDINAL SECTION OF BEECH TREATED WITH TWO COATS OF A HIGH VISCOSITY OLEORESINOUS FLOOR SEAL (MAGNIFICATION $\times 420$)

FIG. 18. TRANSVERSE SECTION OF BEECH TREATED WITH TWO COATS OF A HIGH VISCOSITY OLEORESINOUS FLOOR SEAL (MAGNIFICATION $\times 420$)

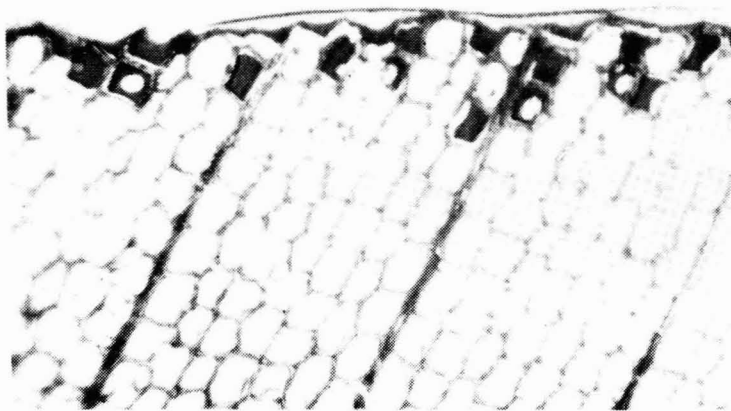


FIG. 19. TRANSVERSE SECTION OF WESTERN RED CEDAR TREATED WITH TWO COATS OF A POLYURETHANE LACQUER (MAGNIFICATION $\times 420$)

of a glued joint. Both he and Plath⁵⁴ have given magnified pictures of sections of glued joints, demonstrating the penetration obtainable. Glues differ from surface coatings in being usually more viscous, and in having considerable pressure applied to them during the setting of the glue.

Photomicrographs illustrating the penetration of various floor seals in Western red cedar (*Thuja plicata*) and beech (*Fagus sylvatica*) are shown in Figs. 15-19. The seals were coloured with an oil-soluble dyestuff before applying two coats to the wood which was stained with a contrasting stain after dry sectioning. These figures tend to indicate the following points:

- (a) The idea of reinforcement of the surface layers of the timber by an oleoresinous seal is only partially true. Penetration of the surface is very irregular and much of the seal which manages to penetrate appears in cells which may be ten or more below the surface, without the intermediate cells being full of seal. This happens in earlywood (Fig. 15) as well as in latewood, and in tangential (Fig. 16) as well as radial (Fig. 15) directions, and it is true even with a polyurethane seal which is not supposed to penetrate (Fig. 19), although in this case the seal does not get quite so far in.
- (b) On hardwoods the seal tends to fill up the vessels in the wood preferentially (Fig. 18).

The detachment of the surface layer of seal in Fig. 19 is an artefact produced during sectioning, but it does demonstrate that the adhesion of the surface layer owes little to the "keying" effect of the seal which has penetrated the wood structure.

It seems clear that the penetration given by "penetrating seals", *i.e.* low viscosity oleoresinous seals, is so sporadic that it cannot have much reinforcing

effect on the wood. The higher viscosity seal gives no less reinforcement, but supplies a thicker surface film in addition. Penetration of all types of surface coating seems to be sufficient to fill up the top cells, particularly if they are broad hardwood vessels, but this does not guarantee good wetting which is the important property required for good adhesion. High viscosity coatings may give reduced wetting merely because they tend to entrap air in the surface, so that the viscosity needs to be low enough to avoid this. Actual penetration of the surface is unnecessary to give good adhesion, though it may be valuable as a surface reinforcement on flooring or in the traditional applications for linseed oil on wood such as cricket bats.

It does seem that the usual instruction of most manufacturers that primer coats of varnish for wood should be diluted is unnecessary in many cases. It is particularly undesirable when the wood possesses good permeability to liquids. High viscosity primers are required

- (i) On end grain surfaces;
- (ii) On plywood and veneers where the fibrous structure of the wood has been loosened;
- (iii) On sawn or other rough surfaces;
- (iv) On quarter-sawn timbers with interlocked or spiral grain. This means, in effect, where there is a large amount of exposed end grain on a surface where it would not normally be expected. This applies to many tropical hardwoods;
- (v) On permeable timber, *e.g.* beech, birch, maple, sapwood of all species.

Low viscosity primer may be necessary with dense impermeable hardwoods and with impermeable softwoods such as spruce (whitewood). The traditional white lead/red lead primer has proved its worth on softwoods (usually Scots pine), but its value is related to other factors besides its ease of penetration, particularly the layer of lead soap which builds up on the surface.

CONCLUSIONS

Quantitative calculations can be made for energy changes during application of surface coatings on wood. Factors influencing their removal are more complex, however, and they have to be discussed in a more qualitative manner. Microscopic examination is a valuable guide to the importance of the various influences.

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REFERENCES

1. Johnson, R. E., *J. Phys. Chem.*, 1959, **63**, 1655.
2. Shafrin, E. G., and Zisman, W. A., *J. Phys. Chem.*, 1960, **64**, 519, and refs. 2-14 therein.
3. Bennett, M. K., and Zisman, W. A., *J. Phys. Chem.*, 1959, **63**, 1911, 1214; 1960, **64**, 1292.
4. McNutt, J. E., and Andes, G. M., *J. Phys. Chem.*, 1959, **30**, 1300.
5. Collins, R. E., and Cooke, C. E., *Trans. Faraday Soc.*, 1959, **55**, 1602.
6. Harkins, W. D., and Feldman, A., *J. Amer. Chem. Soc.*, 1922, **74**, 2665.
7. Harkins, W. D., "Physical Chemistry of Surface Films", (New York, 1952).
8. Cooper, W. F., and Nuttall, W. H., *J. Agric. Sci.*, 1915, **7**, 219.
9. Nuttall, W. H., *J. Soc. Chem. Ind.*, 1920, **39**, 67; *J. Soc. Dyers and Colourists*, 1924, **40**, 104.
10. Quincke, G., *Wiedemann's Annalen II*, 1877, 145.
11. Young, T., *Phil. Trans.*, 1805, **95**, 65.
12. Gans, D. M., *J. Phys. Chem.*, 1945, **49**, 165.
13. Dupré, A., "Théorie Mécanique de la Chaleur", 393, Paris, 1869.
14. Krotova, N. A., Kirillova, Y., and Deryagin, B. V., *Zhur. fiz. Khim.*, 1956, **30**, 1921.
15. Deryagin, B. V., and Smilga, V. P., Paper No. 54, 3rd International Congress of Surface Activity, Cologne, 1960.
16. Leja, J., and Poling, G. W., International Mineral Processing Congress, London, 6-9 April, 1960.
17. Wenzel, R. N., *Ind. Eng. Chem.*, 1936, **28**, 988.
18. Good, R. J., *J. Amer. Chem. Soc.*, 1952, **74**, 5041.
19. Shuttleworth, R., and Bailey, G. L. J., *Discuss. Faraday Soc.*, 1948, **3**, 16.
20. Deryagin, B. V., *Compt. rend. (Doklady) Acad. Sci. U.R.S.S.*, 1946, **51**, 361.
21. Cassie, A. B. D., and Baxter, S., *Trans. Faraday Soc.*, 1944, **50**, 546.
22. Bartell, F. E., and Shepard, J. W., *J. Phys. Chem.*, 1953, **57**, 211, 455.
23. Schwartz, A. M., and Minor, F. W., *J. Coll. Sci.*, 1959, **14**, 572.
24. Bartell, F. E., and Cardwell, P. H., *J. Amer. Chem. Soc.*, 1942, **64**, 494, 1530, 1641.
25. Adam, N. K., *Discuss. Faraday Soc.*, 1948, **3**, 5.
26. Washburn, E. W., *Phys. Rev.*, 1921, **17**, 273.
27. Barkas, W. W., "Wetting and Detergency", 55 (London: A. Harvey, 1937).
28. Zuidema, H. H., and Waters, G. W., *Ind. Eng. Chem.*, 1941, *Anal. Edn.*, **13**, 312.
29. Hare, E. F., and Zisman, W. A., *J. Phys. Chem.*, 1955, **59**, 335.
30. Fowkes, F. M., and Sawyer, W. M., *J. Chem. Phys.*, 1952, **20**, 1650.
31. Kargin, V. A., Konstantinopolskaya, M. B., and Berestneva, Z. Y., *Vysokomolekularnye Soedineniya*, 1959, **1**, 1074.
32. Fry, E. S. J., and Bunker, E. B., *J.O.C.C.A.*, 1960, **43** 640.
33. James, D. M., *J.O.C.C.A.*, 1956, **39**, 39.
34. Fox, H. W., and Zisman, W. A., *J. Coll. Sci.*, 1952, **7**, 428.
35. Cronshaw, J., Myers, A., and Preston R. D., *Biochim. Biophys. Acta*, 1958, **27**, 89.
36. Fox, H. W., Hare, E. F., and Zisman, W. A., *J. Phys. Chem.*, 1955, **59**, 1097.
37. Freeman, H. A., *For. Prod. J.*, 1959, **9**, 451-458.
38. Freeman, H. G., and Wangaard, F. F., *For. Prod. J.*, 1960, **10**, 311.
39. Suzuki, R., *J. Japan Wood Res. Soc.*, 1958, **4**, 156.
40. Allan, A. J. G., *J. Polymer Sci.*, 1959, **38**, 297.
41. Allan, A. J. G., and Roberts, R., *J. Polymer Sci.*, 1959, **39**, 1.
42. Ray, B. R., Anderson, J. R., and Scholz, J. J., *J. Phys. Chem.*, 1958, **62**, 1220.
43. Orchon, S., *TAPPI*, 1958, **41**, 33.
44. Ekwall, P., and Andresen, O., *Paperi ja Puu*, 1958, **40**, No. 4a, 173, 178, 181.
45. Borgin, K., *Norsk Skogindustri*, 1959, **13**, 81, 429.
46. De Bruyne, N. A., *Plastics Institute Trans. and J.*, 1959, **27**, 140.
47. British Standard 373: 1957, "Methods of Testing Small Clear Specimens of Timber".
48. Gray, V. R., *J.O.C.C.A.*, 1960, **43**, 10.
49. Andersson, B., and Nylén, P., Statens Namnd for Byggnadsforskning Rapport 42, "Utomhusfärgen for Trä," (Stockholm, 1957).
50. Suchsland, K., *Holz als Roh u Werkstoff*, 1957, **15**, 385.
51. Browne, F. L., *J. Forest Prod. Res. Soc.*, 1953, **3**, 108; 1954, **4**, 391; *For. Prod. J.*, 1955, **5**, 92, 192; 1956, **6**, 152, 235, 312, 453; 1957, **7**, 145, 248; 1959, **9**, 417.
52. Browne, F. L., and Truax, T. R., Colloid Symposium Monograph No. 4, 258 (Chemical Catalogue Company, New York, 1926).
53. Suchsland, O., *Holz als Roh u Werkstoff*, 1958, **16**, 101.
54. Plath, E., *Holz als Roh u Werkstoff*, 1958, **16**, 467.

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DISCUSSION

MR. G. W. MACK drew attention to the very variable results obtained from weathering tests on wood, variations in the wood and sometimes variations between the woods. For example, in Western red cedar, much worse results were obtained on the darker than on the lighter panels. He understood that the darker wood contained much more extractable matter and less springwood. The extent of replication necessary in comparing different varnishes could be reduced by matching the colour of the panels, but it was not a very satisfactory method and not very quantitative. He asked if some form of spreading test, preferably of a wholly volatile liquid, could be used to obtain more quantitative matching.

DR. GRAY agreed that there was considerable variation in colour between samples of the same timber. Western red cedar varied to a great extent but, nevertheless the A.S.T.M. recommended its use as a standard timber for testing varnish and paint. In his work he had not experienced any serious difficulty from colour variation. The main effect was that darker samples absorbed sunlight more effectively so that the durability of the varnish was increased. Colour was not necessarily associated with the amount of soluble extractives. The amount of natural preservative in Western red cedar was, for example, correlated with light coloured samples. His general experience from weathering tests on varnished wood was that lack of durability was rarely due to poor adhesion. He had not done much work on contact angle measurements, but so far contamination of the surface by extractives did not seem to be important. He thought that a rapid approximate measurement of the contact angle with a suitable liquid might provide a means of determining whether the surface was likely to display poor adhesion. Liquids that altered the surface as little as possible were necessary. For this reason he had used water, acetic acid solutions and, for high surface tensions, concentrated calcium chloride solutions, which could achieve surface tensions as high as 100 dyne/cm.

DR. E. SUNDERLAND said that Dr. Gray had suggested that the reason for failure of varnish systems on wood was simply a question of varnish breakdown, allowing water to penetrate and to hydrolyse the wood surface. In view of contributions to this conference showing that varnish films generally had a high water permeability, he invited Dr. Gray to comment on the alternative hypothesis that breakdown might start by hydrolysis of the surface of the wood, leading to failure of the system before the varnish film had broken down.

DR. GRAY replied that varnish films on wood could be regarded as satisfactory only as long as the colour in the wood remained. In practice this meant that the film must remain intact. Loss of colour took place only when liquid water penetrated in quantity through the cracks in the surface. Passage of water vapour through the film could not supply sufficient liquid water to provide this leaching of the colour. He did not think, therefore, that the permeability of the film to water vapour had any effect at all on the breakdown of the surface or loss of colour.

MR. A. W. LANDMANN, who supported the author with regard to adhesion and penetration, stated that in the work on leather finishing the British Leather Manufacturers' Association had found no correlation between adhesion of the finish and the penetration of the constituents. The effect of "buffing" or roughening of the surface was attributed to cleaning of the surface and an increase in the effective surface area for adhesion, giving a key to the finish.

DR. GRAY said that the main value of slight penetration and roughening of the surface was the increase of the wetted surface area thereby obtained. Penetration in itself was usually not of value. In some circumstances penetration could produce a kind of reinforced rubbery surface layer which gave protection to wear or impact. A traditional example of this was the treatment of cricket bats with linseed oil.

MR. A. G. NORTH said that it had occurred to him that in a polyurethane system there might be a possibility of reaction with the cellulose in the wood, which might affect not only the durability, but also the contact angle. He asked the author whether reaction did take place between isocyanate and wood.

DR. GRAY felt that reaction of polyurethane with cellulose might take place, but that it had no effect on durability since breakdown under weathering was not an adhesion failure. It was probable that chemical reaction took place with the substrate with other types of coating, particularly on metals. He had no evidence concerning the effect of such reaction on contact angles.

MR. R. KERSHAW, commenting on Mr. North's question, said he had no direct evidence that there was reaction between polyisocyanate and the cellulose. It was necessary to recognise that in most woods some of the polyisocyanate would react with the moisture there, and thus it was common practice to use with a certain excess of polyisocyanate.

With regard to adhesion and penetration, he thought that there was support for the view that actual penetration bore little relation to adhesion, certainly in polyurethane systems. He asked whether Dr. Gray had evidence that very thin films of inorganic compounds would be more durable than equally thin films of carbon compounds.

DR. GRAY commented that a glass window provided a remarkable example of a weather resistant transparent polymer and if only a very small amount of its properties could be incorporated into a coating on wood, durability problems would be solved.

MR. J. A. OATES spoke of the importance of the formulator's choice of resins in preparing primers for wood on a two-can polyurethane basis. He said that under-reaction was of importance in sealing coats and the use of higher polymeric additives should be avoided here. Practical experience had shown that absence of adequate sealing under polyurethane varnishes and paints led commonly to poorer adhesion.

MR. R. N. WHEELER asked, since normally only very thin coatings of floor sealers were applied, whether there was practical evidence that they did cement the floor blocks together and fill the somewhat wide gaps that occurred. Further he enquired whether there would be sufficient movement caused by moisture variation in wood block floors to cause them to crack when they were completely covered with a varnish film. Although the varnish film would not be impermeable to moisture, he felt that it must surely exert a considerable stabilising effect which under normal circumstances should considerably reduce moisture variation.

DR. GRAY assured Mr. Wheeler that the adhesion between wood blocks caused by floor seals was a serious practical problem. It happened with all types of seals but was particularly troublesome with the harder types. One possible remedy was to treat the wood block floor before final sanding with a dilute liquid wax. Another was to use a primer with poor tensile strength.

MR. N. R. FISK said it had occurred to him that if a varnish containing any large proportion of glass polymer could be made, it would at least be free from any tendency to embrittlement.

DR. GRAY stated that it seemed that glass fibre reinforced polyester products had good weathering resistance. One of the difficulties of application of glass reinforcement on wood was to obtain a transparent film. A recent development which might assist was the use of a flake glass reinforcing material which could be sprayed with a polyester.

MR. J. D. COHEN, referring to the application of printing inks to paper, said Dr. Gray's characterisation of wood as a low energy solid was particularly interesting.

The figures he had given suggested that oleoresinous vehicles would spread on paper and that aqueous ones might not. This might possibly be a reason for printability defects, such as mottle, which were liable to occur with aqueous inks. He added that wetting agents had not helped satisfactorily so far.

DR. GRAY agreed that water did not spread spontaneously on normal wood surfaces, although it would do so on some timbers immediately after they had been cleaned. This effect was mainly due to contamination on ordinary wood surfaces. He had put forward the straight line relation between $\cos \theta$ and surface tension as a means of assessing the adhesion quality of a surface, whatever liquid was going to be applied.

MR. KERSHAW, referring to the problem of the bond strength of the coating to wood, said that the author had suggested that it should be overcome by using a first coat of low adhesion value, and he wondered whether the author had any practical experience of this, because in the speaker's experience when this was done, failure occurred at the first coat.

DR. GRAY replied that the need was to obtain poor adhesion between the blocks but not on the top surface. The surfaces between the blocks could be treated in manufacture to give poor adhesion.

The Coating and the Substrate

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Summary

The two main reasons for the application of a coating are to protect the substrate against harmful agencies, including mechanical abrasion and the weather, and to modify the physical properties and appearance of the surface. The choice of coating material for a specific application must be related to the properties of the substrate as well as to the qualities required in the coating.

The interactions, both physical and chemical, between the substrate and the coating are considered in terms of specific properties; namely, adhesion, abrasion resistance, durability, water resistance and protection against corrosion.

INTRODUCTION

Unlike the products of many industries, paints, as they are known in the industry, are not finished products, but can more properly be regarded as "intermediates". The finished product is a coating firmly attached to a substrate. This paper presents some ideas on the interaction between physical properties of the coating related to such features as the porosity, swelling propensities, elasticity, reactivity, *etc.*, of the substrate.

In all considerations of painting there is a purpose, and inevitably the substrate is a major factor in these considerations. The two main reasons behind the application of a coating are:

- (i) to protect the substrate against harmful agencies (which can be, for example, mechanical abrasion, chemical attack or sunlight), and
- (ii) to modify the physical properties and appearance of the surface to be painted (*e.g.* colour, gloss, roughness, emissivity, sound absorption, water permeability, electrical conductivity, flammability, *etc.*).

The purpose in the application of paint is to modify the properties of the substrate, but these same properties inevitably influence the process of film formation. The effects are of two main types: porous substrates may absorb either the whole, or selected components of a paint, and reactive substrates may interact chemically with the paint. These interactions, either chemical or physical, may be beneficial, but in some cases may make the achievement of a satisfactory and durable coating difficult.

Clearly, the considerations in painting a smooth, non-porous, essentially non-reactive material such as glass are different from those in painting a reactive metal, a porous plaster or a dimensionally unstable material such as wood. On glass there are no problems of reactivity or of penetration with conventional paint materials, but the smoothness and absence of mechanical key can lead to adhesion problems. With such surfaces it is necessary to develop a strong bond between the coating and the substrate; the problem becomes one of "wetting" and cleanliness of surface.

Metal surfaces embrace a wide range of substrates varying in chemical and physical nature. Smooth and relatively non-reactive metal surfaces, such as chromium plate, are similar in many respects to glass and again cleanliness becomes a prerequisite for good paint adhesion. Clean steel is usually easier

to paint by reason of some degree of surface roughness which can be associated with the nature of the oxide layers, on the surface, *i.e.* the corrodibility of the surface. The efficiency of the coating in controlling the oxidation of the metal surface is the major factor in steel protection by paints. Metals, such as zinc, on which the oxide coating is strongly reactive with components of the paint medium, provide problems of another kind. The reaction products may be brittle and water sensitive and may lead to detachment of the paint film in many circumstances. In such cases it is often necessary to modify the metal surface chemically, possibly by suitable choice of coating material, in order that the undesirable forms of under film products are avoided.

On dimensionally unstable materials, such as wood, the flexibility of the coating materials is important in addition to factors of penetration and bonding. Moisture movement, for example, can cause a good deal of dimensional change in wood to an extent leading to physical breakdown of unsuitable coatings, shown as splitting, cracking and flaking of the paint. Consideration must also be given to the control of moisture movement; relatively impermeable paint systems may be pushed off the substrate as moisture seeks to escape; porous paints may not restrain sufficiently the ingress of moisture so that questions of preservation become paramount.

Initially, it was suggested that a paint material could be regarded as an intermediate and only in conjunction with its substrate could it be properly assessed. For example, a paint based upon oxidisable fatty acid materials may possess excellent film properties in terms of toughness, resistance to destructive agencies, flexibility, *etc.*, and were it to be assessed merely as a paint would pass many tests. Probably it would be totally unsuitable for use on, say, zinc metal, where its components and materials produced during ageing and breakdown would react at the metal surface, possibly causing detachment of the paint film.

Certain properties of paint films are equally necessary on all types of surfaces. For example, it is a prerequisite that all paint films shall firmly adhere and continue to adhere to the substrate. On the other hand, properties such as flexibility may be less necessary on some substrates, *i.e.* the dimensionally stable materials, than on others.

FACTORS INFLUENCING THE DEVELOPMENT OF SPECIFIC PROPERTIES: ADHESION

Paints are applied to substrates as fluids which convert either rapidly or more slowly to solid coatings. For the coating to adhere some bond must be formed between the paint and the substrate; moreover, if there is to be no risk of the coat peeling subsequently, the bond should be at least as strong as the cohesive strength of either the substrate or the paint, whichever is the weaker.

The extent to which a mechanical bond can be developed by penetration into re-entrant pores and crevices of the substrate may be argued. In general, the setting of a paint film involves contraction rather than expansion so that the formation of anything analogous to a simple dovetail joint seems rather unlikely. It is much more likely that the liquid paint may coat the inner wall of a pore channel forming a tubular sheath after drying, which helps to anchor

the coating to the substrate. Such a mechanism would clearly necessitate wetting of the substrate material by the paint; if one accepts this view the requirements for adhesion on a porous substrate do not appear to be much simpler than on a non-porous surface of similar composition, except that the surface area available to form a key may be considerably greater on the porous substrate.

The primary requisite for adhesion on any surface is that the paint shall wet the substrate. Further, as the conversion to the solid film occurs, wetting must be maintained and the cohesion of the film must not be lost. Wetting involves replacement of the molecules of air, water, grease, *etc.*, originally in contact with the surface by molecules of the coating. In many cases, where surface free energy considerations are favourable, wetting is no problem. The rate of displacement of undesired absorbed material depends on the spreading pressure of the paint, the rheology of the paint and the configuration of the substrate. Displacement may be retarded if the paint sets up to a gel with a yield value greater than the spreading pressure or, if air, moisture or other fluid contaminant is trapped in pores or crevices.

Displaced material may be pushed aside, incorporated into the paint or emulsified. In all cases the process is assisted by low viscosity. In order to maintain a low viscosity in a pigmented system, it is normally necessary to use high rates of shear. For this reason application methods such as brushing or the use of rollers are preferable to those methods, such as dipping, which do not involve high shear rates. This consideration applies particularly to priming materials and is less important when a smooth and relatively clean ground has been attained. Solvents are also used to adjust consistency and there is evidence¹ that adhesion is improved as dilution increases, provided that due regard is given to shrinkage effects as the solvent leaves the film. In other words, it is desirable that solvents be chosen to maintain a measure of fluidity in the film for as long as possible.

Removal of moisture from a surface is often attempted by incorporation in the paint of water-miscible solvents. This is often effective in easing application, but does not necessarily result in a coating which is resistant to water². Other methods of displacing water, by the use of surface active de-watering materials, improve the application characteristics, but may introduce side effects in terms of drying, hardness, *etc.*

So far the considerations have been wholly on physical wetting and displacement of contaminating materials at the interface. The other possible approach is to change the surface of the substrate by chemical attack either as a separate pretreatment process or involving components of the paint. Most of the modifications, either by pretreatment or by paints, are by the use of phosphatic materials which clean and etch the surface of metals. Other methods, involving, for example, strong bases, are used as pretreatments, but there is little evidence as yet of the use of basic materials as paint components and surface modifiers, except possibly the amine derivatives which form one class of the surface active materials used as aids to painting on wet surfaces and which are often said to assist adhesion.

Paint types which react and bond chemically with metal surfaces would be expected to develop adhesion forces many times greater than those deriving

from simple physical absorption forces. Etch primers have been shown³ to bond strongly with many metal surfaces, but it is arguable just how much chemical bonding takes place; adhesion figures¹ up to 12,000 lb./in.² have been obtained with etch primers compared with 1,000/5,000 lb./in.² for other types of coating. The success of this approach suggests possibilities in the concept of complexing or chemisorption of organic coatings with other substrates, including wood and plaster.

Some reaction between metal oxides and the acids present in oil, oleoresinous and alkyd systems probably assists in establishing intimate contact on many substrates, such as ferrous metals. The extent of these reactions in simple drying oil films has been shown by determination of the metal content of films immediately after drying on various common metals⁴. At this stage in the development of the film the amounts of metal taken up were 5.2 per cent of lead, 4.1 per cent of copper, 1.33 per cent of zinc, 3.61 per cent of cadmium and 0.12 per cent of iron (from mild steel) (all figures being expressed as percentages of the weight of oil applied). It was noted, incidentally, that application to zinc, cadmium and magnesium markedly retarded drying.

The reaction between simple drying oils and metals is naturally much greater than that for more highly developed media. However, in the course of adhesion tests marked green staining has been observed of the underside of white alkyd paint films stripped from brass; analysis of these films has shown a copper content of 10 $\mu\text{g./cm.}^2$ of surface or, expressed another way, 0.4 per cent by weight on the resin. This amount of copper is equivalent to a layer forty atoms thick over the surface, but such a simple picture is misleading since selective etching would undoubtedly have occurred. However, the figures demonstrate that considerable disturbance of the original surface had taken place.

It is considered that this etching action of drying oil acids and, possibly, the action of acidic oxidation products may be a most important contribution to securing wetting. In particular, it has been found in practice that the adhesion of paints containing drying oil components is less sensitive to very slight grease contamination on metal surfaces than is that of many non-reactive coating materials. On certain metals, however, *e.g.* zinc, cadmium and lead, the nature of the reaction products and the continuing reaction, involving scission products, weakens the adhesive bond between paint and metal. In this connection it is interesting to note that when water is present stearic acid forms metal soap monolayers on certain metallic powders, *e.g.* ferric oxide, Fe_2O_3 , but reacts continuously with others⁵, *e.g.* zinc and cadmium oxide, CdO .

From the considerations of wetting and adhesion, which have been outlined, it might be concluded that adhesion would be easier to secure on a microscopically smooth surface, such as a bright chromium plate, than on a microscopically rough surface, such as abraded steel, and indeed, there is some evidence⁶ to support this. It may be that a greater percentage of the area of the smooth surface is, in fact, wetted by the paint, but in practice, paint is much more likely to strip from a smooth surface than from a rough one. The explanation for this lies in the different distribution of forces in the film and the fact that adhesion failure may be more readily propagated across a smooth surface.

There has been considerable speculation about specific effects on the adhesion of coatings to metals which are related to the possibility of a dimensional "fit" between the atoms of the substrate and the molecules of the coating. Claims⁷ have been made that the adhesion of epoxide resin coatings can be improved by producing on the metal surface oxides of lattice spacing 8-8.5 Å which, it is said, corresponds with the distance between phenol ether groups in the resin chain.

Calculations, based on bond lengths in polymer chains and interatomic distances in crystals, may appear convincing, but if the problem is considered with the aid of three-dimensional molecular models, the picture is rather different. It is soon evident therefore that the flexibility of the skeleton of an epoxide resin of the bisphenol/epichlorhydrin condensate type is such that the distance between consecutive polar groups can be varied between wide limits, to fit equally well on many different metal lattices. In general, taking into account the flexibility of polymer chains and the variety of molecular species found in most paint media, it does not seem likely that interatomic dimensions can greatly influence relative adhesion to specific surfaces.

On the other hand, the chemical nature of the metal surface, particularly the types of oxides and hydrated oxides present, would be expected to control the magnitude of the adhesive forces that could be developed through, for example, dipole association or hydrogen bonding with specific groups in the coating material. Factors of this type could conceivably result in some specificity of adhesion for different paints on different metals.

RESISTANCE TO MECHANICAL DAMAGE

It is proposed to consider here the general subject of resistance to mechanical damage by impact, scratching or abrasion. Only in the case of a coating which is extremely weak in cohesion, owing to, for example, gross over-pigmentation or failure to cure, can mechanical resistance of the film be assessed independently of the properties of the substrate. Generally, performance is governed by at least six factors, namely, the adhesion of the coating material, its cohesion, its extensibility, the elastic modulus of the substrate, the plasticity of the substrate and the rate of deformation. In special cases other properties, including thermal properties, may be important.

The interdependence of the mechanical properties of the coating and substrate is seen very strongly in many types of laboratory tests, *e.g.* Table I shows that the results of scratch hardness tests, using the DEF 1053 Standard apparatus, may vary widely on films of the same paint according to the preparation of the metal before painting and consequent variation in adhesion.

A similar picture could be developed for many other laboratory tests, including impact resistance and bend tests, the results of which are strongly affected by adhesion. Indeed, ideally, in assessing the suitability of a coating for a specific application, the tests should always be made on the nearest possible approach to the substrate/paint film system to be used in practice.

The manner in which the properties of the substrate and the adhesion of the coating can influence the response to stresses has been discussed. The influence of the substrate may be equally important in its effect on the magnitude and distribution of stresses to which the coating is subjected. For instance, a

TABLE I
 VARIATION OF SCRATCH HARDNESS WITH METAL PREPARATION

Paint Ref.	Type	Scratch hardness (g.) on aluminium panel		
		Degreased only	Abraded and degreased	Chromated
A	Ammunition paint	800	1200	1200
B	Oleoresinous primer ..	700	700	1100
C	Vehicle undercoat	500	1500	1600
D	Alkyd gloss paint	750	1500	1750
E	Alkali resistant paint ..	250	750	850

coating on cast iron will never be stretched by more than a fraction of 1 per cent by any elastic vibrations of its substrate, and is unlikely to have to withstand strains of a much greater order, even under impact. Vitreous enamel can, therefore, make an excellent protective and decorative coating on cast iron, whereas its use on a flexible substrate, such as tinplate, would soon lead to failure. In an extreme case, such as that which has been cited, the effect of substrate properties on the possible choice of coating is obvious; in other cases the differences are more subtle, but they should not be overlooked.

One interesting field of use, in which the physics of coating performance still appears somewhat obscure, is that of floor paints. In general, there is not a good correlation between performance in laboratory tests, *e.g.* with the *Taber Abraser*, and practical trials on floors. The problem is not simple; the mechanical behaviour of organic coatings varies with temperature, humidity and with the rate and duration of the application of stresses. It is virtually impossible in a laboratory test to simulate all the variations occurring in practice, and it is unlikely that the same set of conditions will lead to the failure of all types of coatings; for example, one paint may fail by cracking at low temperatures, another may soften at high temperatures and a third lose adhesion in humid conditions. The mechanical properties of the substrate are also important. On a concrete floor very high localised stresses may be set up; on soft wood, stress concentration will be less, but the magnitude of strains may be considerably greater, owing to the deformation of the substrate.

In practice it seems that flexibility, coupled with a rapid response to stress, is the most useful quality for a floor paint⁸ for wooden floors, and that harder films, which may show to advantage on a *Taber Abraser* test, are less satisfactory. On hard substrates, such as concrete, harder coatings may be used satisfactorily, but flexible, rubbery materials still perform well, provided that good adhesion is secured.

RESISTANCE TO COLD CHECKING

The spontaneous cracking, known as cold checking, of some lacquer or varnish films when exposed to cycles involving low temperatures is another example of the interaction of substrate and film properties. The term "cold

TABLE II
COEFFICIENTS OF LINEAR THERMAL EXPANSION

Material	Coefficient (per °C) × 10 ⁵
<i>Substrates</i>	
Oak—along grain	0.49
—across grain	5.4
Mahogany—along grain	0.36
—across grain	4.0
Pine—along grain	0.54
—across grain	3.4
Brick	0.95
Glass (plate)	0.89
Mild steel	1.1
Copper	1.7
Aluminium	2.3
<i>Coatings⁹</i>	
White lead/linseed oil	2.4
TiO ₂ /phenolic varnish	2.8
Nitrocellulose lacquers	3.7-6.8

	Below transition point (T _g ?)	Above transition point
<i>Thermoplastics¹⁰</i>		
Polyvinyl acetate	7.7	23.1
Polyvinyl chloride	6.7	22.3
Polystyrene	7.0	19.6
Cellulose nitrate	8.8	17.1
<i>Polythene¹¹ (25-50°C)</i>	25	
<i>Thermosetting plastics¹²</i>		
Epoxy resins (unfilled)	4.5-6.5	
Glyceryl phthalate (cast resins) ..	5.5-6	
Polyesters (rigid cast resins) ..	5.5-10	

check" is a misnomer in that the form of failure is normally a crack right through the film to the substrate, whereas a "check" is usually taken to be a fissure which penetrates only part way through the film. The basic reason for this failure is that the coefficient of thermal expansion for the coatings is greater than that of the substrates, so that with falling temperatures the coating is increasingly strained. If the extensibility of the coating is low, as it may well be at low temperatures, the strain reaches the level at which cracks occur. On solid wood, where the expansion coefficient varies with grain direction, the crack patterns are influenced by these variations; on uniform substrates, such as glass, the patterns are more regular.

Clearly, if the expansion coefficient of the coating could be maintained nearly equal to that of the substrate, cold checking would be very unlikely to occur. Data on expansion coefficients of coating materials are sparse, but related data for plastics may be compared with those for some common substrates.

The thermal expansion coefficient of *polythene* is anomalous in that it increases steadily up to a maximum of about $50 \times 10^{-5}/^{\circ}\text{C}$ at the melting point (109°C). This behaviour is probably linked with the retention of some degree of crystallinity throughout most of the temperature range between the brittle point and the melting point, the effect of the crystalline configuration being to restrain the normal expansion of the polymer.

Except where otherwise stated, the figures quoted in the table relate to normal atmospheric temperatures. For long chain organic polymers the expansion coefficient changes from a level of $6\text{--}9 \times 10^{-5}/^{\circ}\text{C}$ in the glassy state to about $20 \times 10^{-5}/^{\circ}\text{C}$ in the rubbery state. Fortunately, above the transition point most polymers are highly elastic so that a large differential expansion between coating and substrate does not necessarily lead to failure.

The data quoted refer, essentially, to bulk properties. It is probable that the expansion characteristics and mechanical properties of orientated molecules at the substrate/coating interface would differ markedly from the bulk properties.

However, it is of interest to consider the figures in Table II in relation to temperature changes both in cold check tests and in normal weathering. For instance, in cold check tests it is not unusual to cycle between 50° and -20°C , a range of 70°C . For a nitrocellulose lacquer, with an expansion coefficient of $6.5 \times 10^{-5}/^{\circ}\text{C}$, applied to oak, the differential contraction during the cooling stage of the cycle would be equivalent to 0.42 per cent along the grain and 0.07 per cent across the grain. On this basis, failure would be expected only with a rather brittle film and under conditions of rapid cooling.

RESISTANCE TO WEATHER

Cold checking represents a specific type of failure, which is normally characteristic only of the hard, relatively inelastic lacquers applied in rather thick films to furniture. The failures by checking or cracking which develop during weathering of many types of coating are, perhaps, less directly related to substrate properties. Certainly checking, which is essentially a surface phenomenon, is more likely to be due to a contraction of the surface layer of the coating, than to differential movement of the coating and the substrate.

Cracking, on the other hand, which is a form of breakdown right to the substrate, has often been ascribed to differential thermal contraction.

Are the differential thermal contractions between coatings and substrates, during normal weathering, sufficient to cause cracking? Temperature changes on films exposed to direct solar radiation during the day and to clear skies at night may cover an extreme range of from 50°C above the normal temperature of film formation to 50°C below, a total range of 100°C. Calculations, based on a 100°C change, probably represent some exaggeration of the effective relative contraction from the equilibrium unstrained condition, which is assumed to exist at normal atmospheric temperature. Even so, if the figures for an oil or varnish paint applied to steel are taken, from Table II, the calculation indicates a differential contraction only slightly over 0.1 per cent. For such paints, cracking is usually observed at the stage when the extensibility, as determined by bend tests or tensile tests on detached films, has fallen to a level of 1-2 per cent. It is unlikely, therefore, that temperature change is the direct cause of the defect. Indeed, where cracks develop in films of this type on metals, they can probably be regarded as the ultimate stage in penetration of checking breakdown rather than as a defect originating at the substrate.

When the behaviour of some of the other types of coating is considered, the suggestion that temperature changes cause cracking becomes more plausible. For instance, for some chemically cured resins, such as epoxy resins, and for some linear polymers, such as p.v.a., the calculated differential expansion is greater than 0.5 per cent. Strains of this order might well be sufficient to break some of the more highly cross-linked coating materials; this mechanism may, at least in part, account for the somewhat disappointing weathering performance of cold cured epoxy, urea and melamine resins. Again, temperature changes might provide the final increment of stress required to crack films of some of the linear polymers, including nitrocellulose and polystyrene lacquers, although it is probable that these films only fail after an initial stress has built up as a result of film contraction. Initially, stresses may be set up when solvents leave the film and, later, loss of plasticiser by evaporation, leaching or migration into a substrate may be a factor.

The other element of weather which might lead to dimensional changes in films and substrates is rain or dew. Dimensional changes of wood owing to the absorption of water¹³ are many times greater than those resulting from temperature changes, and are undoubtedly responsible for cracking and adhesion failure of some coatings. Many freshly applied films have a capacity for water absorption and swelling comparable with that of wood. As films age, however, not only does their tendency to swell in water diminish¹⁴, but also their extensibility falls. A stage is therefore often reached when the differential movement sets up a stress sufficient to cause cracking along the grain, *i.e.* at right angles to the direction of maximum swelling of the substrate.

MOISTURE PERMEABILITY

It has been suggested that the durability of paint systems may often be linked with the relative tendencies for the paint system and the substrate to be swollen by water. The ease with which water, and also dissolved salts, can penetrate a film is another important factor.

Permeability may control the protection when a coating is applied to a non-absorbing but corrodible substrate. On absorbing substrates, in particular on wood, a coating can modify the rate of entry or exit of moisture and control the rate of leaching of soluble components. The function of coatings as water diffusion barriers over porous substrates is, however, complex and it is not always clear just what properties are required. In many cases, therefore, as in the first decoration of new masonry, some passage of moisture is desirable. Even in established buildings it may be unsafe to build too good a water barrier in the wrong place, since this may result in condensation and the formation of blisters under the coating.

The permeability of an organic film to gases, including water vapour, may arise from two mechanisms, either hydrodynamic flow through the pores, or diffusion through the body of the film. Flow through pores is not a major factor at pigmentation levels below the critical pigment volume concentration, that is whilst all pigment particles are enveloped in the medium. Permeation by diffusion depends on the product of the diffusion constant, which is related to the size of the diffusing molecule, and the solubility parameter for the diffusing molecules in the material permeated. Gases with a very low solubility in organic media permeate paint films very slowly; water vapour is much more soluble in most films so that relative to other gases its permeation is rapid. Some published data relating to permeability to water vapour, hydrogen, oxygen, ammonia and the inert gases are shown in Table III.

TABLE III
PERMEABILITY OF FILMS AT 20 C¹⁵
(mol. cm./cm.²/atm./sec. 10⁻¹³)

Gas	Membrane			Diameter of gas molecule (A)
	Cellulose triacetate	Polystyrene	Polyvinyl chloride	
H ₂ O	580,000	16,000	4,000	2.72
O ₂	17	—	—	2.8
H ₂	230	—	—	—
NH ₃	2,000	—	—	c2.0
He	225	320	47	1.92
Ne	60	77	11.5	2.35
A	16	12	0.8	2.92
Kr	15	7.5	0.02	3.2
X	2	2.5	0.00	3.5

The water absorption figures quoted for the three membranes were 12–15 per cent for cellulose triacetate, 0.3 per cent for polystyrene and 0.6 per cent for p.v.c. The effect of this degree of solubility on permeation is best shown by the ratios of permeability to water vapour/permeability to neon, which

were 10,000, 200 and 360 respectively, for the three films. The inert gases were assumed not to associate with the molecules of the film and thus to provide a datum level from which the water vapour permeability could be judged.

Clearly no film which absorbs water to a measurable degree can do more than delay the passage of water. For continuous unpigmented films the efficiency of the film in slowing water transport is mainly dependent on its thickness and the solubility of water in the film, *i.e.* the concentration of sites with which water molecules can be associated. In general the lowest permeability is provided by polymers with a minimum of polar groups, as typified by *polythene*. Unfortunately, these polymers tend also to be the most difficult to apply as adherent coatings. Pigmentation may improve the barrier by diluting the film with impermeable solid material and effectively decreasing the cross sectional area of film open to moisture diffusion. Lamellar pigments are especially effective, because they can function at comparatively low volume concentration, so that the risk of development of pores is slight. If the requirements for easy application and good durability are to be satisfied, an acceptable organic film forming material will always have a measurable water permeability. It is to be expected that this permeability to water will be greater than that to most of the water soluble materials present both in and under the film, whether these are ionisable or not. This differential permeability introduces the possibility of osmotic blistering.

As the water resistant qualities of finishing paints have improved, it has become increasingly necessary to take steps to avoid the trapping of salts beneath semi-permeable coatings. Blistering has become endemic on alkyd coach finishes and has generally been associated with pigments which either contain soluble components or form soluble salts by reaction with the acidic products of drying oil oxidation. Indeed, it is questionable whether, in the search for water resistant coatings of high gloss retention, too much convenience in use may not have been lost. It is now argued by some that a safety valve should be built into coating systems for use under damp conditions by the controlled development of pores through the finishing coats. This approach has, of course, been accepted for a long time in the formulation of American and Canadian paints for the exterior of centrally heated wooden houses, although in this case the problem is to control the passage of water rather than that of salts through the film from the substrate.

INTERCOAT ADHESION AND BLISTERING

Blistering in paint systems can arise from many different causes. Some involve the condition of the ultimate substrate; for example, blisters may be caused by the pressure of water, trapped by a paint film in wood or plaster. Blisters may also arise from the effects of corrosion processes on metals, either at anodes or cathodes. However, probably the most troublesome type of blistering is that associated with osmosis. These water-filled blisters usually occur between coats in a paint system, not necessarily at the level where the water-soluble material, which is the primary cause of the defect, originated. The problem of intercoat blistering, which is closely linked with that of the loss of intercoat adhesion by water-soaked films, raises some interesting

questions about the movement of water and dissolved material through paint films.

Osmotic blistering is, especially, a problem with air drying alkyd paints, although it is by no means confined to this type of film. Many unpigmented alkyd resin films when applied to smooth inert substrates, such as glass, will blister after contact with water for some hours, particularly under warm conditions. With unpigmented films the blisters are usually of microscopic size and, moreover, disappear when all the water has evaporated. Blistering of this type is not often serious; it is, presumably, associated with the small proportion of water-soluble organic matter present either in the original resin or developed during the drying process. The blisters are found occasionally as inclusions within a coat, but are usually at the interface, suggesting that there may be some adsorption or preferred distribution of water-soluble material at this level.

When a complete alkyd paint system is exposed to wet conditions a smaller number of much larger blisters sometimes develops. These blisters continue to grow through subsequent cycles of wetting and drying; when the blisters are dissected under a microscope the contents after drying out are found to be water-soluble and either crystalline or gelatinous. In all cases where crystals taken from such blisters have been analysed at the Paint Research Station, the major constituent has been found to be barium, calcium or magnesium formate. Smaller proportions of sulphates, including ammonium sulphate, have also been identified. Formic acid is one of the main products of oxidative scission of linseed oil. It will react readily with many oxides and carbonates to give water-soluble salts. It is of interest to consider, in relation to the mechanics of blistering, the magnitude of the forces which could be developed by osmosis in saturated solutions of the various formates when trapped under a non-porous paint film. The solubilities of a number of metal formates are recorded in Table IV.

TABLE IV
SOLUBILITY OF FORMATES

Metal	g./100 ml. of cold water	m.ol./litre
Barium	27.7	1.2
Calcium	16.2	1.15
Magnesium	7.7	0.63
Zinc	5.2	0.32
Lead	1.6	0.05
Copper (Cupric)	12.5	0.8
Cobalt (—ous)	5	0.32
Potassium	331	36
Ammonium	102	15

If the assumption is made that the salts are completely dissociated in solution the osmotic pressure can be calculated from the number of ions in 22.4 litres of solution. For barium formate the calculated pressure for a saturated solution is approximately 80 atmospheres or 1,150 lb./in.². For lead formate the calculated figure is 3.6 atmospheres or 52 lb./in.².

It is convenient mathematically to consider the equilibrium of a hemispherical blister of diameter d and to neglect the forces required to stretch the cap. This hypothetical blister would grow if the thrust on the cap exceeded the resistance to adhesion loss by peeling offered by the line of contact of film and substrate around the periphery of the blister. The condition for growth therefore becomes:

$$\frac{\pi d^2}{4} \times \text{Osmotic pressure} > \pi d \text{ Peeling force/unit width}$$

or

$$\text{Osmotic pressure} > \frac{4 \times \text{Peeling force}}{d}$$

Peeling forces measured on alkyd films vary from a few pounds per inch width downwards. Assuming a value of one pound per inch width as the peeling force required and an osmotic pressure of 1,000 lb./in.², the calculation indicates that further growth would occur for a blister above a minimum diameter of 0.004 in.; for an osmotic pressure of 50 lb./in.², growth would only occur for a blister above a minimum diameter of 0.08 in.

It must be emphasised that these calculations are based on assumptions which cannot be justified completely, but the factors which have been neglected, such as the stiffness of the coating, would tend to make blister growth less rather than more likely. The conclusion is, therefore, that large blisters would develop only where osmotic pressures were high or over patches of very low adhesion. The first condition appears to be fulfilled in the case where calcium or barium formate is present under an alkyd paint film and the second condition where paint has been applied over, say, a greasy fingerprint. After all the salt under a blister has been dissolved, further swelling of the blister must lead to dilution and a fall in osmotic pressure, which will become inversely proportional to d^3 . An equilibrium size will be reached at which the osmotic pressure is no longer large enough to provide the necessary peeling force.

When in practice the rate of growth of blisters is compared with the permeability of the paint film, it is usually clear that not all the water in each blister could have passed through the blister cap. It is probable that some water, permeating through a considerable area around the blister, travels laterally to the blister, presumably through channels at the interface or through a porous undercoat. Some such mechanism also appears necessary to account for the considerable accumulations of soluble salt which are found in some blisters. It is thought probable that with cycles of wetting and drying, salt dissolved from different parts of the film is gradually sucked into the blister pockets. Ammonium sulphate bloom, in the amounts normally found on paint surfaces, does not appear likely to be a major factor in the blistering of subsequent coats except in so far as the presence of even a very thin and discontinuous layer of water-soluble material must weaken intercoat adhesion¹⁶. Salt crystals left by the evaporation of drops of sea water on ships' paint may

well be of sufficient size to provide the driving pressure for large blisters. Whilst the small, nearly hemispherical blisters developed in or under some paint systems under wet conditions are almost certainly due to osmotic pressure, there is some reason to believe that water-filled blisters can also be produced by differential swelling of the different layers in a paint system. It has been shown¹⁷ that paints of different pigmentation respond differently to water; differences in media also affect both rates and equilibrium degrees of swelling. Where paint films with widely differing response are combined in the same system steep water concentration gradients may result and, in consequence, considerable stresses may develop at interfaces. These stresses could well cause intercoat adhesion failure with blistering or peeling as the stresses relax in the detached film¹⁸.

Undoubtedly, the role of water in the breakdown of painted systems is complex, but several aspects appear to be of major importance. Absorption of water by the paint film, causing dimensional changes which may lead to the development of stress and strain, and the hydrolysis of ester linkages, *etc.*, are likely to be of importance. Water may also diffuse through the coating to the substrate, causing, for example, the swelling of wood or the corrosion of metal, leading to the dislodgement of an otherwise sound paint film. The irregular distribution of water throughout the film may set up internal stresses. This effect may derive, for example, from climatic or weather conditions which cause a paint film to be periodically soaked with rain for many hours and, at other times, to be partially or completely dried out. A comparatively rapid alternation of wet and dry atmospheric conditions would be expected to set up a discontinuous distribution of water throughout the paint film thickness, and the resulting erratic dimensional changes might be expected to induce a corresponding variation in the stresses and strains developed in the film. In this way a paint film may, under appropriate conditions, behave differently over its area and throughout its thickness, so that only certain areas fail or breakdown may not penetrate the whole film thickness.

RESISTANCE TO CORROSION

The need for studies on paint films to embrace the composite systems of paint film and substrate is, perhaps, best illustrated by reference to the protective functions of paints on metals. Such considerations go well beyond those implied in the introduction, which briefly mentioned the physical character of the metal surface and its possible chemical activity. Corrosion processes are different for different metals and inhibitive systems for one metal cannot necessarily be used on others. It is, therefore, common practice to study anti-corrosive behaviour of paints only on the appropriate substrate. There are, however, many ancillary studies made on detached films which would, it may be argued, be more informative and reliable if the total system of substrate and coating formed the test specimen.

It was shown by Mayne¹⁹, for example, that paint films were so permeable to oxygen and water that they were unlikely to prevent these elements reaching the metal surface. Indeed, the permeability of a wide range of films to these materials was shown to be great enough to support the corrosion of metals at a rate similar to that if the metal substrate were exposed without the benefit

of a coating. The interpretation of such findings could suggest that the application of paint films to metals did nothing to delay the onset or retard the rate of corrosion. It is, however, well known in practice that the interposition of almost any paint film between a metal surface and the environment has a marked inhibitive effect. The deductions as to the permeability of the membranes studied were made on films unsupported by a substrate, and it is fair to suggest that the ability of surface coatings to protect in practical situations, *i.e.* when they are applied to the surface, is in some way due to the inter-relationship of the coating material and the base to which it is applied. Furthermore, when permeability studies are made on unattached films it is usual to establish an artificial concentration gradient across the films so that the moisture vapour or other gas is driven through the film under a form of pressure. On many substrates such a pressure or gradient is unlikely to be present and, in any event, when it is present is unlikely to be as steep as that used to obtain accelerated effects in laboratory work. Some caveat must be entered on osmotic effects, leading to blister formation, but even here the need for careful interpretation following laboratory studies is necessary, for many films which blister in the laboratory tests do so to a much lesser extent in practice.

These are the kinds of situations which bedevil attempts to study film characteristics and properties divorced from matters relating them to the basis material. Such properties as adhesion, chemical interaction, selective penetration, *etc.*, are factors which are not normally taken into account when unsupported films are examined or studied. The situation appears to be such that deductions drawn from work on unattached films when interpreted and applied to paint films in practice are of doubtful validity. They can only be applied safely when there is precise information regarding the inter-relationship of the applied film and the particular substrate. Water absorption and permeability studies of paint films are always difficult, owing to the continual change in the physical character of the film as the water is taken up, which, in itself, changes the permeability and absorption characteristics. A film tightly held to a substrate may be tolerant and flexible enough to withstand moisture movement without visible signs of rupture but, in some cases, detachment or other failure may occur. In any event, unless the nature of the film is such that repair of ruptures on a self-healing basis is possible, the system is strained in such a way as to detract from the mechanical properties and protective qualities of the film. Detached films, unchecked in their movement by attachment to a substrate, may give few indications of likely failure to remain attached to a substrate or of a possible tendency to break, crack or otherwise lose a protective screening effect for a substrate.

The mechanisms by which paint films protect metal substrates to which they are applied have been the subject of a great deal of study at the Paint Research Station and elsewhere. For simplicity, two main types of protection are envisaged, although they are not always mutually exclusive. The exclusion of corrosive elements is broadly considered as resistance or barrier inhibition and any interference with the electro-chemical processes of corrosion, deriving from the paint system, is termed chemical inhibition. At the Paint Research Station a valuable tool used in this work has been an electrode potential study technique²⁰ in which metal panels, coated over half their area, were scanned with a travelling electrode. The potentials at regular intercepts from the

boundary between painted and unpainted areas were recorded and plotted. Curves obtained from these plots were basically S-shaped and deductions were made about the significance of variations in size and distortions in shape of the curves obtained. Compression of the curve was thought to show a higher level of protection by the exclusion of corrosive materials and distortion of the curve to show interference with either or both of the electrode reactions, according to the position of the distortion.

Most of the studies were made on painted steel specimens from which it was deduced that red lead conferred both anodic and cathodic protection. Calcium plumbate was also shown to interfere with the anodic and cathodic electrode reactions, but the major inhibitive property appeared to lie in the effect on the cathodic reaction. Red iron oxides, chromate pigments, white lead, basic lead sulphate and lead cyanamide gave no indication of anodic or cathodic inhibition, but the studies indicated that their resistance inhibitive properties varied greatly. Chromate pigments have been used for many years in anti-corrosive paints and it was thought that they behaved as chemical inhibitors by their influence on the anodic reaction. It was, therefore, surprising that in the electrode potential studies on steel there appeared to be no direct effect on the electrode reactions with the chromates used (Fig. 1). The studies showed, however, that chromates could provide anodic inhibition on some non-ferrous metals (Fig. 2), aluminium being the one chosen for study²¹. It should be noted that failure to interfere with the electrode reactions does not necessarily rule out the possibility of some forms of chemical effect leading to corrosion inhibition. For example, reaction between basic pigments and acidic components of the medium can change the structure of the paint film and in neutralising the acidic materials may change the corrosive potentiality of the system.

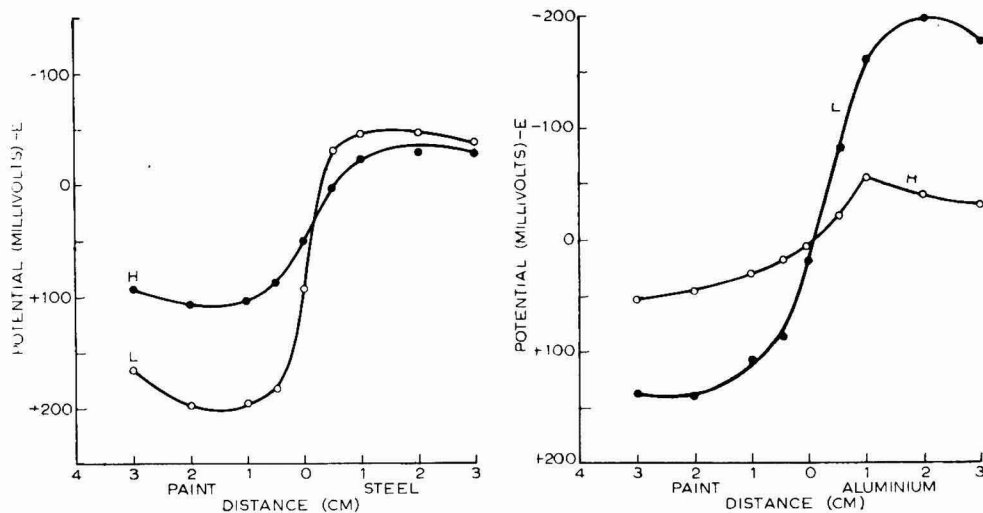


FIG. 1. POTENTIAL DISTRIBUTION BETWEEN STEEL AND ZINC CHROMATE
(H—high solubility, 62 μ ; L—low solubility, 82 μ)

FIG. 2. POTENTIAL DISTRIBUTION BETWEEN ALUMINIUM AND ZINC CHROMATE
(H—high solubility, 25 μ ; L—low solubility, 32 μ)

It was noteworthy in the results found for chromates on steel that the more soluble the chromate pigment used, the better was the resistance inhibition. This suggests that the mobile ions in the chromate pigments are in some way changing the barrier status of the paint system. One possible explanation is that ferrous materials leaving the corroding metal surface are oxidised at the interface between paint and metal, or within the paint film, and that the ferric components so formed impede the further passage of ions in both directions. The different mechanisms shown by chromate pigments on ferrous and non-ferrous metals is an indication of the importance of the combined substrate/paint system, if the inter-relationships are to be fully investigated and understood.

METAL COATED STEEL

The variety of forms of metal coated steel provide interesting examples of how the physical form of the metal coating, with the attendant chemical features, can influence the painting requirements. Aluminium, lead, tin and zinc are all used as forms of cladding for steel but, perhaps, the most widely used metal coating for steel is zinc in various forms. The painting of zinc or zinc coated steel, where the zinc presents a continuous surface, is often difficult, owing to poor paint adhesion initially, or the failure to maintain adhesion in service. Initial failure of paint adhesion is normally due to the greasy, smooth character of the surface, which prevents good wetting by the paint. The subsequent forms of failure, leading to flaking and peeling, result from interaction between the zinc surface and acidic components of the paint vehicle, which produces a brittle, water sensitive layer between the paint film and the metal²².

Sprayed metal coatings are quite porous and take up most forms of paint quite easily. This porosity, however, gives rise to some doubt that the conventional paints for zinc metal offer the best approach to painting zinc sprayed steel. There is a basis for the belief that sprayed metal coatings can act as "filters", allowing the medium to penetrate whilst holding back unbound or underbound pigment near the surface of the sprayed metal. When this happens the finishing paint system is liable to premature chalking, owing to the removal of that portion of the binder required to wet out "filtered" pigment. There must also be a possibility of poor adhesion of the finishing coats if such wetting out is not satisfactorily achieved.

The selective penetration of media into metal sprayed systems was examined by applying a number of pigmented and unpigmented systems of various viscosities to grit blasted and metal sprayed *Perspex*. Small pools of the paint were placed on the specimens which were turned over at intervals and the penetration of the medium observed through the transparent substrate. It could be seen by the gradual darkening observed on the under sides of the specimens. The rate of penetration was, as would be expected, governed by viscosity and in the cases of the pigmented systems used little colour appeared to accompany the medium. It was clear that some separation of the paint was taking place within the pores of the sprayed metal coating which, in turn, suggested that relatively unbound pigment remained near the surface. That some effect of this kind was to be expected had been deduced from observations

on examples of painted metal sprayed work in practice. In one case newly zinc sprayed coatings had been protected by a pigmented primer, followed by an undercoating and finishing paint in light battleship grey. When examined some six weeks after completion of painting, intensive loss of gloss had occurred and chalking of the surface was well advanced. The paint system was of a type which, at the time, was much favoured by the Admiralty and was not in ordinary conditions notable for early failure by chalking. It was then thought possible that selective penetration of the medium had occurred from the primer and that medium from following coats had been taken up to wet out the primer pigments, leaving the final coat deficient.

Conventional primer media are usually dependent on oxidation for drying, and produce scission products which are acidic. These, together with acidic materials in the medium, can attack a zinc surface even in the massive form. The much greater (approximately five times) surface area of sprayed zinc coatings increases the tendency towards reaction and such attack within the structure of the sprayed coating can weaken it to an undesirable extent. More reliable results have been obtained when the sprayed metal is first coated with a non-oxidising material or when etch primers, of rather higher solids and lower phosphoric acid content than normal, are used, so that the reaction on the zinc surface is deliberate and controlled. The relatively weaker acids formed in the oxidative drying of subsequent paints are then less likely to attack and disrupt the metal coating.

PENETRATION INTO POROUS SUBSTRATES

As has been indicated already, one of the ways in which a substrate can most clearly modify a coating is by absorption of either the whole paint or selective portions of it. The study of paint behaviour on porous substrates is complex and cannot usefully be discussed in detail without reference to both the physical and chemical nature of specific substrate and coating materials. However, there are some basic concepts which may be mentioned. Provided that the liquid paint wets the walls of capillary pores, suction forces inversely proportional to capillary radius will be set up. Flow into the capillary will continue unless or until:

- (a) the capillary is blocked by solid material, such as a large pigment particle,
- (b) the paint gels to give a structure with a yield value equal to the capillary force,
- (c) air or solvent vapour trapped in a closed capillary is compressed to a pressure which balances the capillary force.

Blockages by pigment particles are usually not complete and may often form a filter bed through which the fluid vehicle can penetrate. For instance, if red lead primer is applied to an unglazed ceramic tile of very fine pore size, the oil will penetrate leaving a layer of almost dry pigment behind. On a tile with much larger pores there is some penetration by the whole paint, but the residue on the surface retains the normal oil gloss characteristics. With emulsion paint systems, where three phases are present, namely, pigment, binder and water (possibly with dissolved thickener), behaviour on porous substrates can be more complicated. The whole paint may penetrate, pigment may be filtered

out, or the aqueous phase may penetrate leaving capillaries blocked by the binder which has been thrown out. Where, as in oil bound water paints, the binder is also liquid this may also penetrate selectively.

It is not easy to study these phenomena on the normal painting substrates, such as plaster, but at the Paint Research Station useful results have been obtained by using banks of sheets of selected filter papers as model substrates. This technique has the advantage that the substrate can be sectioned readily, simply by separating the sheets of paper, and the relative penetration of the various elements can then be assessed. This approach has proved valuable in investigating the influence of such factors as the viscosity of media and the pigmentation, on the ability to form continuous, adherent films on various types of porous substrate.

PAINTED SURFACES

When coatings and substrates are considered, the tendency is to think first of the application of paint to metals and building materials. The foregoing discussion has, indeed, been largely concerned with the problems arising in this connection. However, it must be recognised that the most frequently painted substrate by far is, in fact, a paint film. This paint film may be the residue of a previous painting system or merely the preceding coat in a new system. Many of the considerations which have been discussed in relation to the painting of other substrates relate equally well to repainting. For example, wetting can again present problems, a specific case being the difficulty of repainting over some silicone containing materials. Equally, the same requirements of cleanliness and freedom from salts and excessive moisture apply.

In addition to the normal problems of dirt, grease and moisture there may be the additional problem of moulds or algae on the old surface, especially where conditions are particularly favourable to the development of such organisms. Recognition of such contaminants not only calls for extra care in cleaning, but also indicates the desirability, in extreme cases, of modifying the coating material by the addition of appropriate fungicides.

In repainting over a weathered paint film, account must be taken of the mechanical condition of the film and its relation to the ultimate substrate. If the film is chalking, there may be difficulty in wetting it sufficiently to bind the old and new films together. If the adhesion of the old paint has suffered, the application of the new film may be all that is necessary to disrupt the bond to the substrate. The first effect may be that solvents from the new paint swell the old gel, possibly causing portions of it to curl or wrinkle. Later, as the solvents evaporate, both new and old films may shrink, causing a build up of stresses which finally overcome adhesion. The low molecular weight products of oxidative drying may also be highly active in these swelling and shrinking processes. Clearly, when there is good reason to suspect the adhesion of the old paint, *e.g.* when flaking or open cracking has developed, every attempt should be made to remove the previous coat before repainting. When the old paint appears to be firmly attached to the substrate, but has possibly become underbound and somewhat brittle, the first coat of new paint should contain a rather higher proportion of medium than is necessary for new work. The most dangerous condition is when a paint, pigmented up to the critical pigment

volume concentration, is applied over old paint which has become brittle. In such a paint contraction stresses on drying develop most rapidly and reach the highest levels.

Reference has already been made to problems of intercoat adhesion. It is clear that in some of these problems the time sequence of painting is involved. For instance, adhesion between the undercoat and finishing coat of an alkyd system may be sound if the coats follow each other within a few hours, but poor if several days elapse between their application. This behaviour seems, at least in part, to be due to the nature of the fully dried paint surface, because considerable improvement can often be effected by rubbing down with abrasive paper between coats. Whether the problem is essentially a matter of wetting, or merely the existence of too sharp a dividing line between regions with different mechanical properties and response to water, remains to be determined. It might be expected that a chemical bond would be developed between successive paint coatings based on materials containing drying oils, in view of the considerable amount of residual unsaturation remaining in the dried film. However, the difficulty may be associated with the strongly hydrophobic nature of the fully dried surface, which suggests that there may be a high degree of orientation or an exudation from the gel of a fully saturated component. Intercoat adhesion failures rarely occur from paint films which are soluble in any of the components of the succeeding film, neither do they occur from undercoats based on oxidative media, when the finishing coat is applied early enough for "sinkage", as manifest by low gloss, to take place. The inference is that, in these cases, inter-penetration of the two coats has effectively bound the films together.

CONCLUSIONS

The examination of surface coatings for use on particular substrates or for particular conditions of use depends to a large extent on laboratory test methods. These are adopted for convenience, speed and opportunity for detailed examination and appraisal. Often the substrate eventually to be used is not available in suitable form for use in the laboratory, or some condition of the test method makes it imperative that detached films, or suitable specimens attached to convenient substrates, shall be used. It is surprising how successful the surface coating industry has become in its ability to develop materials for specific conditions, often far removed from the precise conditions under which the examination of potential coatings is made in the laboratory. It speaks well for the interpretative skill of the technologist and his instinctive or deductive reasoning, in that such development is nearly always eventually successful, although occasionally a number of false starts may be made or optimistic views taken which may have to be modified later.

The paint film should be considered as a protective system placed between the given substrate and the environment in which, in the painted form, the system has to survive. It is not advisable to consider these three elements of the system, the substrate, the environment and the coating, separately, because their inter-relationships in service are inextricably bound together. The success or failure of a paint coating depends on factors arising from substrate behaviour and the effects of the environment. It has often been said that the failure of a paint film is due to a conjunction of circumstances. It is often apparent that

had a substrate been a little better prepared, or had the paint film been a little thicker, or had the environment been a little less aggressive, then the life of the system would have been adequate. Usually a system has a sufficient tolerance to cater for one deficiency. When, however, a further weakness, possibly in some other element of the system, occurs then the probability of failure is multiplied.

The most unusual and surprising choice of coating for a given substrate and given conditions will sometimes survive. This is a happy situation for the fortunate user, but the paint manufacturer is not particularly interested in a one per cent success and is particularly concerned with a one per cent failure. His view must be a statistical one and he must design his systems, with recommendations as to where and when they are to be used, to give a minimum risk of failure.

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REFERENCES

1. Malloy, A. M., Soller, W., and Roberts, A. C., *Paint Oil Chem. Rev.*, 1953, 18, 14.
2. James, D. M., *J.O.C.C.A.*, 1960, 43, 391.
3. P.R.S. Technical Paper, No. 205.
4. P.R.S. Research Memo., No. 175.
5. Lancaster, J. K., *Trans. Faraday Soc.*, 1953, 49, 1090.
6. Alter, H., and Soller, W., Amer. Chem. Soc., Div. of Paint, Plastics and Printing Ink Chemistry, New York Meeting, 1957, 17, 2, 356.
7. U.S.P. 2,934,456.
8. Talen, H. W., and Brunt, N. A., *Verfkroniek*, 1950, 23, 236.
9. P.R.S. Technical Paper, No. 88.
10. Calculated from volumetric measurements of Clark, R. F., and Rynkiewicz, L. M., *Ind. Eng. Chem.*, 1944, 36, 279.
11. Hahn, F. C., *et al.*, *Ind. Eng. Chem.*, 1945, 37, 526.
12. "Modern Plastics Encyclopaedia".
13. U.S. Department of Agriculture, *Wood Handbook*, 1940, 197.
14. P.R.S. Technical Paper, No. 162.
15. Muller, F. H., *Kolloid Z.*, 1942, 100, 355.
16. P.R.S. Technical Paper, No. 208.
17. P.R.S. Technical Paper, No. 191.
18. James, D. M. (private communication).
19. Mayne, J. E. O., *Research*, 1952, 5, 258.
20. Bharucha, N. R., *Nature*, 1960, 187, 4739. 756.
21. P.R.S. Research Memo., No. 287.
22. Whitby, L., *P.R.S. Bulletin*, No. 34.

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DISCUSSION

MR. R. R. DAVIDSON asked what was the function of the ammonium ion, and secondly he referred to blisters which were produced in accelerated weathering. Soluble soaps such as formates could readily be leached from primer films under weatherometer or blister box conditions. It thus appeared that such films were permeable to soap ions. He asked if it were justified to treat the films as semi-permeable membranes, permeable only to water, as was done in the paper.

MR. RUDRAM replied that Dr. J. B. Harrison had published an article dealing with the importance of the ammonium ion in corrosion attack by the atmosphere; he had found strongly held ammonium material at the surfaces of metals.

MR. BULLETT, referring to Mr. Davidson's second question, thought that the fallacy in the argument concerning permeability arose from the fact that a paint could not be regarded as a homogeneous material.

When weathering began the surface of the paint film began to break down; it gradually became porous in the upper layers. However, the bulk of the film still formed a semi-permeable membrane. Osmotic blisters under single coats were small and often collapsed as weathering proceeded. Larger blisters were involved when the undercoat contained the reactive material.

MR. H. F. CLAY expressed the view that the part of the paper dealing with corrosion was fundamentally unsound. A solution of 4 per cent of water in triacetin, used as the corroding environment in the original work at the Paint Research Station, was not corrosive, and steel completely immersed in the solution did not corrode; the explanation was that oxygen was insoluble in this solution.

He continued by describing some simple experiments which seemed to show that the solution did not corrode because oxygen was excluded. When an L-shaped strip of steel was partially immersed in triacetin, with the vertical limb extending into the air, after a few days a large patch of thin rust had developed on the under-side of the horizontal portion. This indicated that the controlling factor in the corrosion of the partially immersed specimen was the supply of oxygen, rather than the conductivity of the solution, the oxygen promoting the cathodic part of the reaction. In a second series of experiments four pieces of aluminium were placed in test tubes and a little mercury was added to each. In the first tube the aluminium was exposed to air, while water was added to the second. Triacetin was added to the third to cover the specimen completely, and to half cover it in the fourth.

In the first and second tubes the metal was attacked quickly, whilst in the third and fourth there was no attack. The corrosion of aluminium in contact with mercury was no doubt due to the oxidation of the aluminium from the amalgam which must form between the aluminium and the mercury; and the fact that this couple did not corrode in triacetin could only be explained by the insolubility of oxygen in triacetin, so that oxygen could not get to the amalgam. Mr. Clay asked what solution was used in the tests described in the paper, and whether the authors had worked with aqueous solutions.

MR. RUDRAM replied that for some years Mr. Clay had disagreed with the technique employed, and it seemed as if this would continue. Mr. Clay was conversant with the relevant work at the Paint Research Station; when they had duplicated his tests they had not been able to obtain the same results. They had found that the triacetin solution used corroded both aluminium and steel; he agreed that in a corrosion process oxygen availability was likely to be a significant factor.

MR. CLAY illustrated the shape and dimensions of his specimens. He repeated that it seemed that the supply of oxygen rather than the conductivity of the solution was the controlling factor.

MR. RUDRAM replied that the rate at which corrosion occurred at paint/metal boundaries depended largely on the particular pigments used. In support of the technique he pointed out that the results accorded with practical experience in most cases. The largest potential differences occurred at the paint/metal junction which normally coincided with the more or less vertical portion of the curve. The whole system would vary considerably across the boundary. He said that he was interested that at the bottom of the L-shaped specimen there was in fact corrosion in view of the emphasis placed upon oxygen availability.

MR. G. W. MACK agreed that the Taber Abraser was misleading for assessing floor paints. Since the paper was written, he said, National Building Study Research Paper No. 32 had been published, dealing with the forces exerted by the foot in walking and providing a basis for what was hoped to be a more satisfactory test. While admitting the desirability of matching the coefficient of expansion of paint and substrate for thin panels, such matching might be undesirable on thicker substrates. Extreme temperatures were usually short lived, and the mass of material, unchanged in temperature, was sufficiently strong and rigid to resist bowing in a building. Good adhesion and long-term flexibility, including the relief of stress by creep, seemed likely to be more important than matching coefficients of expansion.

MR. RUDRAM thanked Mr. Mack for his reference to the new standards for the examination of these materials. He added that, although the authors had mentioned briefly the thermal mechanism, they had rather attributed failure to other mechanisms.

MR. Z. KALEWICZ asked if there were any relationship between the water absorption of a given paint system and the adhesion to various substrates (steel, zinc, copper, brass and glass), and, secondly, whether any investigations had been made to determine the possibility of modifying the fatigue strength of metal substrate (steel machine parts, *etc.*) by using various coatings.

MR. BULLETT replied that the Paint Research Station had carried out some work on the correlation between water absorption and adhesion failure, but they had found that it was not decisive, for the reason, he thought, that there was considerable stratification in a paint film. They had found that when specimens were immersed in water, the strength of adhesion fell much more quickly than the rate at which the water absorption equilibrium was approached. They had not investigated the problem of fatigue strength and had no statement to offer.

DR. N. A. BRUNT said there were serious objections to the notion of adhesion conceived in some of the papers presented to the conference. This was quite clearly apparent from the following simple experiment. A strip of a viscoelastic paint was applied to a smooth surface, *e.g.* a glass or a metal plate, in the ordinary way. After drying, the plate was mounted horizontally and one end of the strip was detached from the substrate. The free end, hanging down, was loaded with a small weight (a few grams), and it appeared that the film was detached from the substrate at a steady rate. For small loads the rate was very slow (several microns per second). From experiments carried out at the research laboratories in Delft, the rate of detachment could be represented by an exponential function:

$$V = C \exp \left[- \frac{\epsilon}{kT} \right]$$

V being the rate of detachment, C and ϵ were constants and k was the Boltzmann's constant. The value of C depended on the elastic energy stored in the film, and ϵ represented the amount of that energy. Thus for viscoelastic materials the notion of "force of adhesion", defined as a force per unit of surface or per unit of length, did not exist. For each rate of detachment and for each temperature there was an appropriate force.

The following was an interpretation of the fundamental relation mentioned. At the edge of the tear, where the process of detachment took place, a certain amount of elastic energy was stored and was balanced by the energy of adhesion. It could be proved that for each of the contact-making atoms in the region of the adhesion tear there were two equilibrium positions, separated by an energy barrier of height ϵ . The quantity ϵ was, in a first approximation, equal to the energy of adhesion and could be determined from a plot of $\log V$ versus T . The elastic energy stored at the edge of the tear was proportional to $\frac{1}{2} \sigma^2/E$, σ being the stress and E the modulus

of elasticity, which was, of course, very sensitive to plasticisers of all sorts, such as swelling agents, and also to water. This explained why all soft materials had poor adhesion and why hard and brittle materials had good adhesion. If a paint layer were wetted it would swell, and E was decreased by a factor varying from 10 to 100. Consequently, for the same load and stress σ , the rate of detachment was greatly increased, resulting in poor adhesion. After drying, the adhesion was re-established. The real forces of adhesion were, of course, the same in both cases, and only the mechanical properties of the material were affected by the wetting.

MR. BULLETT thanked Dr. Brunt for his very interesting exposition which he did not entirely accept, but he felt that it was inappropriate to enter into further discussion.

DR. J. A. W. VAN LAAR referred to his contribution to the Fifth FATIPEC Congress, concerned with the mechanisms of blistering. He said that when painted steel sheet was partly covered and exposed to free water, blisters were at least partially formed electro-osmotically. Preference was shown for blistering along uncovered spots and also at the corresponding areas at the back of the panel, where secondary anodic and cathodic spots developed due to atomic hydrogen, resulting from the primary corrosion and diffusing through the steel. As shown by Wirth and Machu, blisters generally developed at cathodic spots on the metal surface, provided that the paint film had a negative charge. If painted steel were made cathodic by electrical means, blistering would be more severe.

The movement of the water might also account for the pronounced swelling of paint films on metal, water being transported in one direction preferentially. When regarding blisters one was often convinced that a blister had developed from the build-up of the pressure of water drawn to some cathodic spot (either natural or induced) on the metal. The blister was a segment of a sphere. This did not need to be in conflict with the fact that no water emerged when the blister was punctured. Of course, the film was swollen, and the adhering film would be under tension. However, the film deformation was plastic to a large extent and the modulus of elasticity was rather high. The electro-osmotic transport of water explained the localities of the blisters.

MR. G. TENGSTRAND asked how the surfaces of the panels were prepared before painting and further whether the paint was applied by brushing, dipping, spraying or roller. He said that in Sweden there was a standard method of preparing the surface and that most test panels were prepared according to that specification, which he felt was very necessary. The Corrosion Committee of the Royal Swedish Academy of Engineering Sciences, who had specified the standard, had also undertaken careful research on the problem. The Committee had found that the preparation of the surface was a most important consideration in the painting of iron and steel.

Mr. Tengstrand then showed a series of coloured slides to illustrate his arguments. He said that if a *Talysurf* or similar instrument were employed, the picture of the surface obtained was sometimes a false one. He considered the use of a microscope to be more satisfactory. By sand blasting, which was found to be the best surface preparation, "valleys and hills" were always formed; it was necessary for the first coat to fill the one and for the second coat to protect the other. He said that the slides would show how the preparation of the surface increased the effect of the brushmarks, and how the thickness of the film would vary. One of the slides showed a steel panel cleaned by usual methods and painted by brush; the red lead primer had actual contact with about only 10 per cent of the steel. Another of the slides showed that a more uniform coat was achieved by spraying on a sand blasted surface.

With regard to the subject of blistering, Mr. Tengstrand supported Dr. Gray's view of the mechanism; he felt that it was not the presence of water alone which was important, but rather the presence of soluble salts.

MR. RUDRAM said that the authors supported Mr. Tengstrand's views that the preparation of surface and methods of application were of prime importance. The slides shown to illustrate his points were most effective and they were aware, from other information, of the meticulous care with which Mr. Tengstrand prepared his specimens for study in the microscope. His work, and that demonstrated in the excellent series of corrosion studies of other Swedish workers, firmly underlined the importance of surface preparation.

Throughout the paper there were direct or implicit suggestions as to the importance of substrate/paint relationships which were, of course, determined by the ability of the paint to make contact with the true substrate, *i.e.* its state of preparation, and to the need for displacement of air, moisture or other contaminants which directly related to the method of application and the shear forces involved.

The authors considered that Mr. Tengstrand's remarks supported many of their own views, and they felt that his original questions were almost rhetorical for they were fully answered by his illustrations.

MR. H. R. HINDLEY (in a written contribution) said that the authors suggested differential thermal expansion between the coating and the substrate as the cause of cold-checking. That was probably correct, but did not explain why failure occurred after a number of cycles, and not on the first cycle. Some change must take place in the film, perhaps crudely analogous to fatigue or cold working in metals. He asked whether the authors knew of any work on this topic, or on another which might be relevant, *i.e.* stress relaxation in coatings at different temperatures.

THE AUTHORS replied that Mr. Hindley had raised a point which had been worrying many people for some time. In some cases one could postulate gradual embrittlement during cold-check cycles as a result of the evaporation of retained solvent or volatile plasticiser, but there were other films which did not contain volatile components yet failed reproducibly after a number of cold-check cycles. That behaviour did suggest an analogy with fatigue effects in metals, but in view of the structural differences it would be dangerous to press the analogy too far. One possibility was that the first cold cycle might produce cracks at a sub-microscopic, almost molecular, level, which grew during subsequent cycles until they become visible. In that connection it was pertinent to refer to the considerable volume of work done on the stress-crazing of plastics, such as polystyrene and polymethyl methacrylate. It had been shown (Russell, E. W., *Nature*, 1950, 165, 91; Maxwell, B., and Rahm, L. F., *Ind. Eng. Chem.*, 1949, 41, 1988) that those plastics developed a surface craze if strained to a small extent, 0.7 per cent for polystyrene, at a temperature below the brittle point or second order transition temperature. The rate of growth of the craze pattern increased with temperature up to the transition temperature, *i.e.* crack propagation continued faster under the same general stress at higher temperatures. It might well be that the warming part of a cold-check cycle played some role in developing cracks.

On the more general subject of stress relaxation and possible fatigue effects in surface coatings, a great deal could be said. The mechanisms and thermodynamics of stress relaxation were covered, for example, by Tobolsky in "Properties and Structure of Polymers" (New York: John Wiley & Sons Ltd., 1960). Relaxation times could vary from fractions of seconds at temperatures well above the brittle point to centuries at temperatures well below this point. The relations between stress and strain for cyclic stresses were complex at all times, and when a varying temperature was included, they must almost defy analysis. It was not unlikely that the net effect after a number of cycles might be cumulative. There was a little evidence for fatigue failure of organic films (*e.g.* by Roberts and Jobling in "Rheology, Theory and Application", Vol. II, 532), but considerably more work was required.

DR. D. CANNegiETER said that in the authors' paper, and in that of Dr. V. R. Gray (*J.O.C.C.A.*, 1961, **44**, 756), the problem of paint blistering had been discussed; in both papers the formation of blisters had been explained by high pressure. The authors had even calculated osmotic pressures of about 80 atmospheres. In Holland, Dr. N. A. Brunt had published an article (*Verfkroniek*, 1960, **33**, 93) in which he expressed serious doubts about the high pressure theory. If a blister were pricked, it did not contract, neither did water spurt from the hole. He pointed out that blisters were only formed when the paint or varnish film was in contact with liquid water.

If the height of the blister was h and the radius r , then the enlargement of the surface was given by

$$\frac{\pi(r^2 + h^2)}{\pi r^2} = 1 + \left(\frac{h}{r}\right)^2$$

If the linear swelling was λ , then the surface enlargement due to swelling would be $(1 + \lambda)^2$, which was approximately equal to $1 + 2\lambda$. Equating the two equations for surface enlargement, it was found that

$$\frac{h}{r} = \sqrt{2\lambda}$$

In practice,

$$\frac{h}{r} = \frac{1}{5}, \text{ i.e. } \lambda = 2 \text{ per cent.}$$

Dr. Brunt estimated λ for different paints and varnishes and compared the results with the behaviour of the paints in the "blister box". He found in all cases that no blistering occurred when $\lambda < 1$ per cent, and that blisters were formed when $\lambda > 2$ per cent.

Dr. Cannegieter stated that he had also carried out some tests himself and had found similar results to the above. In addition, he had found that the swelling, λ , was influenced by (a) the pH of the water, the higher pH value giving a larger value of λ and more blistering; and (b) the pigmentation: in the table below a relationship is given between λ and the type of pigmentation for several paints made from the same alkyd vehicle at a PVC of 30 per cent, with water at pH 7 and pH 5.

Pigment	λ (%)	
	pH 7	pH 5
Zinc oxide	5	—5
Red lead	5.5	3
Lead titanate	3	—
Zinc chromate	21	21
Zinc tetroxychromate ..	7	7
Whiting	6.5	9

Dr. J. van Loon, during his study of paints on wood, explained the phenomenon of blistering by the diffusion of water vapour through the wood and subsequent condensation under the cooler surface of the paint film, leading to swelling of the film and blistering. In his paper, Dr. Gray came to the same conclusion and gave

the same possibility for cure as Dr. van Loon, *i.e.* that good painting of the inner surface of the wood prevented diffusion of the water vapour and consequently blistering on the outside. In fact Dr. Gray recommended, in his paper, painting the inside of wooden structures with aluminium paint. However, Dr. Cannegieter said that he could not agree with Dr. Gray with respect to the high pressure mechanism of blistering.

Dr. van Loon had found that in most paints swelling decreased on ageing. Paints which swelled when they were still fresh did not swell at all when they were about one year old. In experiments with a "blister house", some paints blistered very badly in the first winter; during the next summer the blisters disappeared when the film had dried out, and in the second winter, in similar conditions to the first, no blistering occurred. This confirmed the hypothesis that blisters were formed only by swelling of the paint film in liquid water. The pressures were as great during both winters, and, according to the pressure theory, the paint should have blistered during the second winter as badly as during the first one.

It was also well known that blisters never burst during their formation, and if they were caused by high pressures, it might be expected that the paint film would occasionally be stretched beyond its elastic limit, *c.f.* the Erichsen Test. The authors had found salts, mainly formates, in the blisters and had deduced that high osmotic pressures explained the blistering. Dr. Cannegieter said that a further possible explanation might be that, by hydrolysis of the formates, the pH of the solution under the paint film was increased, with the result that further swelling occurred.

The authors had also discussed the intercoat blistering in paint systems, which they again attributed to osmosis. However, if it were assumed that blistering was caused by swelling, a further explanation was possible. If for the primer $\lambda < 1$ per cent, and for the top coat $\lambda > 5$ per cent, the primer would not blister on the substrate, although the top coat would blister on the primer. Intercoat blisters would be formed more easily because of the decrease in intercoat adhesion in the water-soaked film. Dr. Cannegieter thought it remarkable that the authors persisted with their osmotic pressure theory, having admitted (page 800) that water-filled blisters might be produced by differential swelling by layers of film. In conclusion, Dr. Cannegieter felt, although much further work was needed, the determination of the swelling of paint films in water of variable pH values would give valuable insight into the phenomenon of blistering.

THE AUTHORS replied that Dr. Cannegieter's exposition of the swelling theory of blister formation was very persuasive, but they were not convinced either by his contribution, or by Dr. Brunt's article, that swelling was the whole or, indeed, the prime cause of blisters. They would consider the questioner's various points in turn.

(i) The fact that water did not spurt from a pricked blister was not proof that pressure was absent. Very little energy was stored in a small volume of liquid under a few atmospheres pressure, so that the kinetic energy of water emerging from the blister could only be derived from the elastic strain in the paint film; moreover this energy transfer would be retarded by the not insignificant relaxation time of the film. That some pressure must be present had been demonstrated by James (*J.O.C.C.A.*, 1960, 43, 653). He showed that when blisters developed on thin, painted metal foils, part of the blister profile was observed on the metal side; in Dr. Cannegieter's view this could be explained only by swelling of the metal or by contraction of the paint film.

(ii) The authors agreed that water-filled blisters only formed when the film was in contact with liquid water, although this water might be no more than a discontinuous layer of condensation. They had found, however, that blistering did not occur in solutions exceeding critical molar or ionic concentrations. For example, a particular long oil alkyd film did not blister in solutions of concentrations of 4 per cent sodium chloride or 15 per cent glycerol (corresponding to internal pressures of about

30 atmospheres of dissolved ions and 36 atmospheres of dissolved molecules respectively). Blisters formed in distilled water collapsed in about two hours after transfer to the solutions and reformed on returning to distilled water. The addition to the alkyd of 5 per cent of calcium formate raised the glycerol concentration needed to suppress blistering to 20-25 per cent (48-60 atmospheres, comparable with the osmotic pressure of a saturated calcium formate solution).

(iii) The surface enlargement which the authors had observed in paint blisters was often much greater than the 4 per cent quoted by Dr. Cannegieter. Thus on one test panel four blisters gave h/r ratios of 0.61, 0.45, 0.65 and 0.66, corresponding to a mean linear extension of 17.4 per cent, much more than the linear swelling to be expected from the particular type of paint.

(iv) So far, the authors had found little effect of pH on the water absorption by films in stirred water, but they were re-examining this point more carefully. However, the considerable effect of pigment content on absorption, similar to that reported by Dr. Cannegieter, had been found. The striking increase in swelling which he reported for films containing zinc chromate, a pigment of comparatively high solubility, suggested that some form of internal blistering connected with pockets of dissolved salt might be occurring. The authors had observed effects of this kind in certain unpigmented alkyd films which rapidly turned milky after immersion in water. Under high magnification the milky appearance was seen to be due to small spherical regions of low refractive index and, presumably, of high water content. Dr. Mayne had demonstrated similar effects.

(v) Some intercoat blistering was undoubtedly linked with the presence of soluble salts. The authors had no evidence of a high pH value except in the special case of cathodic blisters; normally, the contents of blisters containing calcium and barium formates were about pH 7. It was possible that the initial intercoat adhesion failure at the blister site might be associated with stresses due to differential swelling, but they believed that the growth of the blister was largely due to osmosis.

(vi) Dr. van Loon's findings, that blistering tendencies decreased with paint age, would be confirmed by most paint technologists. The authors believed this to be due to an increase in porosity to a level at which the film no longer functioned as a semi-permeable membrane. The increase in stiffness of the film on ageing also made the development of blisters of large h/r ratio unlikely, whilst decrease in adhesion favoured larger and flatter blisters when any build up of pressure occurred.

In conclusion, the authors felt that no one had a complete explanation of, or cure for, all sorts of paint blisters. There was scope for more research by both the "swelling" and the "osmotic" schools, and probably for the application of both theories in appropriate situations.

DR. V. R. GRAY, to whom part of Dr. Cannegieter's remarks were directed, stated that the formation of blisters by paint and varnish films could not take place without internal pressure. It was true that the swelling of the film in water and the fall in adhesion of the swollen film influenced blistering, but without the internal pressure they could only produce film detachment. Such film detachment had been observed with an alkyd varnish in a wet situation, with alkyd epoxies and polyurethanes when end-grain wood surfaces transmitted moisture beneath a film, and with paint on a window frame. Such films were irregular in shape, in contrast to blisters which were almost circular. The extent to which they were circular was in fact an indication of the importance of internal pressure in their formation.

Paint films did not possess long-term elastic properties capable of withstanding pressure. They flowed until stresses were relieved, so that the absence of pressure in a blister was no proof that there had been none initially. Similarly, bursting was

not to be expected, since thinning of the film caused by blistering would increase its permeability so as to relieve the pressure to the extent, sometimes, of the presence of small pinholes.

With porous substrates such as wood, vapour diffusion caused by a thermal gradient could cause condensation of liquid water beneath the film. Swelling of the film and loss of adhesion could cause irregular film detachment, but blisters must involve additional internal pressure, such as that caused by solar heating of the outer surface too rapidly for the vapour to diffuse through the film or the substrate. Swelling of the film obviously would enhance this effect, but the films which swelled also transmitted water vapour readily, so that a clear correlation between swelling and blistering would not be expected. Dark films which absorbed radiation, and so became hotter, were more prone to blisters than light films. Impermeable films, such as an aluminium primer, were for that reason inclined to blister, and permeable films, such as those given by emulsion paints, were regarded as blister resistant, and were therefore used extensively on exterior timber in North America.

Dr. Gray said that he had not seen details of Dr. van Loon's work, but his observation that paint blistering was less in the second winter than in the first could be explained as readily by the greater vapour permeability of films subjected to a blistering cycle as by ageing in swelling properties.

Reviews

MOON BASE—TECHNICAL AND PSYCHOLOGICAL ASPECTS

By DR. T. C. HELVEY. New York: John F. Rider Publishing Co. Inc., 1961. London: Chapman & Hall Ltd., 1961. Pp. 72. Price 18s. 6d.

This is a short book within the space of which the author has attempted an appraisal of the technical problems likely to confront human beings setting up a base on the moon. To some extent the problem of sexual and psychological adjustment is exaggerated, particularly for brief journeys, but the problem is there and cannot be ignored for longer periods of isolation. However, the book is written in a style which uses scientific jargon for the sake of effect. On page 43, for example:

“Channelling of unavoidable sexual and hostile energies into areas of usefulness to the mission is a basic requirement. Libidinal energy may even have the function of incrementing the performance of certain individuals. Hostility, although recognised as irrationally derived, could be nurtured by such an individual as a promoter of his over-all drive level. In any case, the alleviation of detrimental effects resulting from sex tensions and hostile tendencies should not preclude examination of their basic origin as a continuous function of insight”.

A style such as this is difficult to understand and far from enjoyable to read. The discussion of the project may be of some use to those technically involved in space programmes, but this book would not please the general reader.

J. B. ECKERSLEY.

THE EXPLORATION OF THE SOLAR SYSTEM

By F. GOODWIN. London: Chapman & Hall Ltd., 1961. Pp. 200. Price 42s.

This book, written by a young man not yet twenty, attempts to outline the development of astronautics over the next one hundred and fifty years. It is obviously the expression of the young author's all-consuming interest in the subject. For the reviewer the book crystallised a number of the vague notions that the layman has about space and the possibilities there are for man in his eternal quest for truth, allied to the chance of great adventure, which is an important facet of man's nature that needs engaging.

The book is well presented and abounds with facts and figures. Obviously one cannot chart the future without speculation, but the reviewer found this to be well controlled with every regard to the known facts. For anyone interested in detail about the exploration of space, this book is well worth reading.

J. B. ECKERSLEY.

TELOMERISATION AND NEW SYNTHETIC MATERIALS

By R. KH. FREIDLINA and SH. A. KARAPETYAN; translated from the original by M. F. MULLINS; edited by B. P. MULLINS. London: Pergamon Press Ltd., 1961. Pp. 102. Price 25s.

This book is an account of some of the important work done in the U.S.S.R. in the field of telomerisation reactions and their use in the preparation of

new organic intermediates for the manufacture of synthetic fibres and other products. The book begins with a brief introduction to polymerisation, after which the authors present a simple approach to the theory of telomerisation. This is followed by a chapter on the technology of telomerisation, which is devoted exclusively to the production of tetrachloroalkanes from the reaction of ethylene with carbon tetrachloride, together with a description of a pilot plant for operating this process. Subsequent chapters outline the synthesis of other intermediates from tetrachloroalkanes and give a detailed description of the production of the new synthetic fibre *Enanth* (Nylon 7), the properties of which are compared with those of other polyamides.

The book is written for the reader with a knowledge of school chemistry and will probably have a somewhat limited appeal. As a review for the research worker it lacks references to original work, although some are quoted at the end of the book; work done outside the U.S.S.R. receives little credit.

Unfortunately, some errors were noted in the text, such as the statement that high temperatures were necessary for the production of polyethylene at high pressures, and the misnaming of a thiol group as a thio group. The book itself is produced by a non-letterpress setting and photolithography, in the interests of early publication and economy.

J. W. SPOORS.

SURFACE ACTIVITY

By J. L. MOILLIET, B. COLLIE and W. BLACK. London: E. & F. N. Spon Ltd., 1961. Second Edition. Pp. xvi + 518. Price 75s.

Since the first edition of this book was published ten years ago, considerable advances have been made both in the academic and practical aspects of surface active agents. This second edition has been expanded and brought up to date and now covers published literature up to early 1960.

It is a book which will be of use to all concerned with surface coatings, covering in a clear and concise manner the physical chemistry, technical applications and chemical constitution of surface active agents in three distinct sections. Parts Two and Three will obviously be of most interest.

Part Two describes wetting out and waterproofing processes, emulsification and demulsification, the dispersion of solids in liquid media and detergent processes. Unfortunately, the treatment of the dispersion of solids in non-aqueous media is dealt with relatively briefly, due to the lack of published information, there being less than twenty references cited.

Part Three, covering the chemical constitution, is excellently written, and trade names are only mentioned where absolutely necessary in the description of chemical processes in connection with patents.

This book would be an asset to any technical library, not only because of its contents, but also because it is a "readable" book, with references at the foot of each page. Its cost, by today's standards, makes it good value for money.

D. S. NEWTON.

GAS CHROMATOGRAPHY ABSTRACTS, 1960

Edited by C. E. H. KNAPMAN. London: Butterworth Publications Ltd., 1961. Pp. 200. Price 42s.

This book is a third volume of the series of abstracts sponsored by Gas Chromatography Discussion Group. The 1958 volume contained 1,468 abstracts, the 1959 volume 717 abstracts; the 1960 volume contains 875 abstracts.

The list of journals from which the abstracts were made is quite imposing—it contains 128 titles. Thirty-five abstractors, including many prominent writers in the field, abstracted these journals during 1960. This volume, as well as the previous ones, includes an author index and a detailed subject index. The latter includes seven principal classes, such as general articles, theory, definitions and retention volume data, apparatus, carrier gas and column packing material, sample type, applications and specialised separations, and finally related methods and techniques. Each class contains several subdivisions.

These three volumes contain a nearly complete bibliography of gas chromatography and, although the abstracts sometimes do not give a clear picture of the usefulness of the paper, at least the important papers cannot be missed as nearly the whole field of journals is covered.

The reviewer found that many of the papers appearing in various journals contain repetition of the same work and it would be perhaps useful in the new editions if some method of stressing the most important papers could be adopted by the editors of this useful publication.

S. M. RYBICKA.

A CHEMIST'S INTRODUCTION TO STATISTICS,
THEORY OF ERROR AND DESIGN OF EXPERIMENT

By D. A. PANTONY. London: The Royal Institute of Chemistry, 1961. Pp. ii+38. Price 5s.

In the introduction it is stated that "this monograph is intended to assist the beginner by acting as a glossary and by giving elementary mathematical derivations and examples, so that he can use . . . (standard) books to greater profit". The title suggests a wide coverage of statistical methods, and indeed the author contrives within the narrow compass of the publication to include them all.

However, it cannot, nor is it intended to, stand on its own. The development from section to section is not always logical and consists rather of short accounts of the various topics. The treatment is mathematical and would probably assist students (which includes all those seeking to master statistics), if used in conjunction with books on methodology, to fill in the mathematical basis as each new aspect is reached. In this respect, the booklet is commended as a good concise account of mathematical statistics and should be extremely useful to those who wish to fill the gap between the uses of statistics and theory without undertaking extensive mathematical reading; however, it is unfortunate that formulae 4, 5 and 8 are incorrectly printed. The booklet also contains six fully worked examples which illustrate the theories given.

H. R. TOUCHIN.

EDITORIAL

A. I. P. T.?

Most members of the Association will have read by now that the Study Group on Technical Education of the Paint Manufacturers Co-operation Committee has recommended the formation of an *Education Advisory Centre*, *Publicity* on what the industry has to offer in scientific careers, the establishment of a *Paint Industry Education Fund* and of a *Professional Qualification*. The first two of these recommendations have been accepted by the industry, but it appears to have taken nearly two years for the industry to make up its mind on these, the less controversial of the suggestions. The Report of the Study Group was completed in eighteen months, a commendable effort in view of the complexities, but it appears that a further two years were necessary for consideration before the Report was published. We hope that widespread interest in the Report will accelerate the conclusions on the second two recommendations and, more important, their implementation. The subject is vital to the industry, and every year counts, as potential technical staff are lost to more active branches of the chemical industry. How many companies can honestly say that the quantity and quality of technical effort have grown in even direct proportion to the growth in production over the past thirty years—in an industry which claims to be replacing craft by science?

Naturally, the recommendation of most direct interest to this Association is the fourth. Since this is still *sub judice* it may be inappropriate to make suggestions editorially, but our correspondence columns are open. Perhaps as important as the establishment of a Professional Qualification is its recognition by employers. There are still those who consider that there is *no* equivalent to a University Degree, just as there are some to whom *City and Guilds* is a rather nasty word. If there is to be a Professional Qualification, then let it be one which can and will demand universal recognition. But what about Printing Inks?

COMMENT

A semi-technical publicity film can never be easy to produce since a balance has to be achieved between that which is not too technical to be of interest to the general public, and that which is not too blatantly advertising to command the attention of more scientific audiences. LAPORTE TITANIUM LTD. have satisfactorily struck such a balance in a film which they have recently completed. We understand that it is to be shown throughout the country during the next few months and we cannot refrain from mentioning its first, we believe, public screening at a meeting of the Southern Branch of the London Section in October.

The film runs for nearly half an hour and is partly in black and white, finishing in colour. Black and white may not be inappropriate for the story of processing from ilmenite to titanium oxide and there is some very worthwhile photography, particularly in the opening sequences showing the mining and transport of ore. Equally memorable is a colourful closing kaleidoscopic display indicating end uses of TiO_2 . Sufficient recommendation for the film is probably found in the fact that interest is sustained throughout the half-hour and even the most critical viewer can hardly complain with any justification of a blatant or discordant emphasis.

Information Received

(In case of difficulty regarding addresses, members and subscribers to the Journal should apply for details to the General Secretary of the Association at the address shown on the front cover.)

The formation of a new company—NOSS MAYO DISPERSION PRODUCTS LTD.—has been announced. The company will specialise in the production of high quality dispersed materials. Initial production is devoted to the manufacture of colour dispersions for use in the paint, printing ink and plastics industries.

The Paints Division of I.C.I. LTD. has developed and introduced a non-aqueous phosphating process known as *Kephos*, which is stated to dispense with rinsing and tank heating and to form no sludge in the processing tank. The process is suitable for application by dip, brush, roller, spray or flow coating methods. The Dyestuffs Division of the same company has announced the introduction of *Monolite Fast Scarlet RNS* in a granular form, which should facilitate handling of the pigment. The granules are cylindrical and approximately $\frac{1}{4}$ in. \times $\frac{1}{8}$ in.

PARKINSON COWAN MEASUREMENT have recently announced the availability of new brochures describing their comprehensive range of liquid metering and dispensing equipment, including *Types S, 22, 33*, and the *Unipulse* meters, together with their range of *Rotoplunge* pumps.

A leaflet received from the General Chemicals Division of I.C.I. LTD. gives details of an addition to the company's range of metal degreasing plant. This consists of their standard degreasing plant with a built-in lift to give semi- or fully-automatic working.

A Russian report entitled *The Location of the Vegetable Oils and Fats Industry* has been translated and published in booklet form by JOSEPH CROSFIELD & SONS LTD., from whom copies may be obtained.

A recent edition of *Inklings*, published by COATES BROTHERS LTD., is devoted to the subject of fluorescent inks. Many difficulties preventing the use of such inks have now been overcome and the article describes their successful commercial application by letterpress, gravure and offset methods.

F. W. BERK & CO. LTD. have announced that they have acquired Greensplat China Clays Ltd., who own deposits of high grade china clay in the St. Austell area. Grades suitable for the paint, paper and ceramics industries will be distributed through the Company's Head Office in London, and through provincial offices in Manchester, Glasgow, Swansea and Wolverhampton.

WALKER CHEMICAL CO. LTD. of Bolton have asked us to notify readers that their new telephone number is 23264.

LAPORTE CHEMICALS LIMITED, a subsidiary of Laporte Industries Limited, has entered into an agreement with the Spanish company, Peroxidos S.A., to provide technical assistance and advice on the construction of an autoxidation hydrogen peroxide plant near Saragossa in Spain. The initial capacity of the plant will be 1,000 tons of hydrogen peroxide annually (calculated as 100 per cent), production planned to start in 1963, subsequently rising to 1,500 tons.

London Section

SOUTHERN BRANCH

RECENT EXPERIENCE WITH POLYURETHANE VARNISHES AND PAINTS

The first meeting of the current session was held on 25 September at the Royal Hotel, Southampton, when a paper entitled "Recent Experience with Polyurethane Varnishes and Paints" was delivered by Mr. J. A. Oates.

The speaker commenced the lecture by reviewing the theoretical background associated with manufacture of polyurethanes and gave examples of the use to which media of varying degrees of complexity may be put. The need for understanding the differences in surfaces of various timbers was emphasised so as not only to design a varnish for wood but to make due allowances for the porosity and grain of the particular substrate concerned. Examples of resin blends were given, covering the range of wood finishes from floor varnishes to yacht finishes.

Mr. Oates explained some of the difficulties involved in pigmenting polyesters. Owing to the poor wetting properties of the resin, really intensive grinding was needed to obtain good results. Pigments and fillers used must be inert to the polyurethane reaction and if exterior exposure was concerned, topcoats should not contain more than 40 per cent pigment calculated on the binder to ensure the greatest possible freedom from chalking. It had been found that most pigment dyestuffs gave improved fastness to light in a polyurethane binder.

For the final section of his lecture, the speaker returned to the subject of varnishes, in particular the one-can polyurethanes. The principles of manufacture were explained together with the attendant difficulties, the main one being the exclusion of moisture necessitating the use of anhydrous solvents. The lecture ended with the first showing in this country of a superbly produced film which presented the apparently limitless uses of polyurethanes in a most convincing manner.

During the discussion which followed, Mr. Oates dealt ably with the various questions put to him. Mr. J. Hawkins, in proposing the vote of thanks, made reference to the apparent temerity of manufacturers in this country in using polyurethane coatings, considering the great advances made recently. Mr. J. Kingcome seconded the motion and thanked Mr. Oates for his excellent paper, which had set a high standard for the coming session.

A. F. R.

Victorian Section

ANTI-FOULING PAINTS

The Fourth Technical Session for 1961, which took place on 3 July, consisted of a paper entitled "Anti-fouling Paints", by Mr. F. Marson, of the Defence Standards Laboratories.

The speaker stated that the term "fouling" was generally applied to the effect of various marine animals and plants which attached themselves to underwater objects. Settlement only occurred on stationary or nearly stationary surfaces, which meant that ships' bottoms could only foul when the vessels were docked or anchored. Fouling organisms found in the waters of Sydney harbour included algae, barnacles, tube worm, watersipora and bugula.

The main effect of fouling was that it increased the roughness of hull and propellers, thus increasing hull resistance and reducing propulsive efficiency. The resistance of a ship to passage through the water was based on two main components: skin resistance, which predominated at low speeds, and residual resistance due to wave formation

and eddy currents, which predominated at high speed. Skin resistance was increased by fouling and also by the roughness due to the paint films applied to hulls. Minimum initial total resistance would be given by a fully welded hull with faired seams, coated with a smooth, glossy paint. The resistance increased as leaching and deterioration of the paint occurred, and also as plates became buckled in service and pitted by corrosion. The Royal Australian Navy estimated that the fouling of ships cost £A 200,000 per annum, made up of increased fuel consumption and docking costs.

The history of fouling and its prevention went back 2,000 years to the Phoenicians, who used pitch and copper sheathing on ships' bottoms to deter "the worm". British Admiralty reports of 1758 mentioned copper sheathing and it was in general use over wooden and steel hulls until the late 1800s, when electrolytic corrosion proved the system to be highly undesirable.

By 1865, three hundred patents for anti-fouling paints had been issued in England alone. In the main these were entirely useless and anti-fouling paints had a bad reputation for many years. From the 1900s, three basic types of anti-fouling paints emerged, which were:

- (a) Shellac-based U.S. formulation with mercuric oxide as the toxin (1908-22).
- (b) Rosin-based anti-fouling paints (1911-21).
- (c) Hot plastic formulations using coal tar rosin.

All effective anti-fouling paints operated by the gradual release of toxins, which poisoned the larvae of the fouling organisms at their settling stage. The existence of two release mechanisms was recognised, being the matrix-soluble and the contact leaching types.

The lecturer described new techniques of measuring leaching rates and the development of an accelerated method of test. He concluded with a discussion on paints tested or developed at the Defence Standards Laboratories.

K. R. B.

SCIENTIFIC LIBRARY METHODS

The subject of the Fifth Technical Session, held on 7 August, was "Scientific Library Methods", the speaker being Mr. P. Russell, C.S.I.R.O. Library, Canberra.

Owing to the rapid progress of science in the last century, large quantities of recorded knowledge had accumulated. There was a tendency for over-emphasis on the role of laboratory and other experimental work, whereas the use that research workers made of previous achievements was often disregarded.

One of the principal tasks of a special or industrial library was to collect, analyse, classify and place at the research worker's disposal the latest knowledge recorded in the literature.

An important basis of specialist libraries was a well-considered and selective acquisition policy. This was dependent on the clarification and limitation of the sphere of collection. In turn, the collection sphere was determined by the given field of specialisation and by the objects of the organisation concerned. The decisive criterion of the acquisition policy was the indicator showing the usage of the library stocks.

The lecturer then discussed classification and cataloguing. The increasing number of scientific journals had caused many difficulties for research workers which were solved to some extent by abstracting journals. A further trend was seen in the new journal *Chemical Titles*, which indexed using a keyword prepared with a computer, and the use of the "Minicard" system of indexing.

The speaker concluded his paper by discussing possible future methods of communicating scientific literature and he suggested ways and means whereby the enormous quantities of scientific literature could be kept within useful and usable bounds.

K. R. B.



[Photograph by

REUNION DINNER

Lawson & Co.]

Standing (left to right): Mr. J. McKie (*Ass. Sec.*), Mr. P. M. Haigh (*Rep. West Riding*), Mr. R. H. Hamblin (*Gen. Sec.*), S. G. Clifford (*Hon. Sec. & Treas.* 1925-29), Mr. N. A. Bennett (*Pres.* 1957-59), Mr. J. A. F. Wilkinson (*Pres.* 1932-34), Mr. A. A. Drummond (*Hon. Ed.* 1929-31), Mr. R. P. L. Britton (*Fdr. Mem. & Hon. Sec.* 1929-30), Mr. T. Hedley Barry (*Hon. Ed.* 1924), Dr. R. F. Bowles (*Hon. Ed.* 1947-54), Mr. H. Gibson (*Rep. Scottish Section*), Mr. H. R. Touchin (*El. Mem.*), Mr. F. Sowerbutts (*Hon. Treas.*).

Seated back row (left to right): Mr. C. Allsop (*Ch. West Riding*), Mr. H. J. Northeast (*Rep. Midlands*), Mr. N. H. Seymour (*Ch. Midlands*), Mr. F. Cooper (*Vice-Pres.*), Mr. G. Copping (*Hon. Ed.* 1933-37), Mr. G. N. Hill (*Hon. Ed.* 1942-46), Mr. J. A. L. Hawkey (*Vice-Pres.*), Dr. J. B. Harrison (*Hon. Res. & Dev. Off.*), Dr. L. A. Jordan (*Pres.* 1947-49), Mr. G. A. Campbell (*Pres.* 1934-36), Mr. S. Marks (*Guest of Honour*), Dr. H. A. Hampton (*President*), Mr. C. J. A. Taylor (*Guest of Honour*), Dr. J. N. Friend (*Pres.* 1922-24), Mr. P. J. Gay (*Imm. Past Pres.*), Mr. H. Gosling (*Pres.* 1953-55).

Seated at left table (left to right): Mr. A. Aitkenhead (*Ch. Bristol*), Mr. H. R. Wood (*Fdr. Mem.*), Mr. A. Z. Molteni (*Fdr. Mem.*), Mr. S. Sharp (*Rep. Hull*), Mr. C. W. A. Mundy (*Pres.* 1955-57), Dr. S. H. Bell (*El. Mem.*), Mr. I. C. R. Bews (*Hon. Ed.*), Mr. L. O. Kekwick (*Pres.* 1951-53).

Seated at right table (left to right): Mr. J. Smethurst (*Rep. Manchester*), Mr. V. C. Thompson (*Rep. Bristol*), Mr. A. W. Ayres (*Vice-Pres.*), Mr. H. Smith (*Ch. Manchester*), Mr. A. A. Duell (*Rep. Newcastle*), Mr. A. W. Blenkinsop (*Ch. Newcastle*), Mr. A. T. S. Rudram (*Ch. London*), Dr. A. J. Seavell (*El. Mem.*), Mr. R. N. Wheeler (*Rep. London*), Dr. H. W. Keenan (*Pres.* 1944-47). Also present but not in the photograph: Mr. A. J. Gibbon (*Pres.* 1938-40).

Reunion Dinner of Past Presidents, Past Honorary Officers, Founder Members and Council

On the evening of 4 October, members of Council had the pleasure of receiving eleven Past Presidents, seven Past Honorary Officers, together with two Founder Members, at the Wax Chandlers' Hall for the Annual Reunion Dinner. Also present on this occasion were Mr. C. J. A. Taylor and Mr. S. Marks, the Editors-in-Chief of the

Association's Technical Training Manuals, to whom presentations were made to mark the appearance of the first of the Manuals.

After the Loyal Toast the President, Dr. H. A. Hampton, first reminded those present of various Association activities which had taken place since the last Reunion Dinner. At the end of the year



[Photograph by

Lawson & Co.]

The President (*Dr. H. A. Hampton*) presenting a gold watch to Mr. C. J. A. Taylor (*one of the Editors-in-Chief of the Paint Technology Manuals*) watched by (*from left to right*): Mr. I. C. R. Bews (*Hon. Editor*), Mr. S. Marks (*the other Editor-in-Chief, who received a Murphy portable radio*) and Dr. H. W. Keenan (*Chairman of the Technical Education Committee*).

two new Sections had been formed, in Auckland and Wellington, from the old New Zealand Section and it was understood that the new Sections were making good progress. Meanwhile, the United Kingdom Sections had not been inactive and two Branches of Sections had been formed, one known as the Southern Branch of the London Section and the other as the Irish Branch of the Bristol Section. The Association's Conference at Torquay had been very well attended, the standard of papers was high and the discussions lively.

At the Annual General Meeting in Torquay, Honorary Membership was conferred on Mr. G. Copping, a Past Honorary Officer.

The Paint Manufacturers' Joint Executive Council had released a Report on Technical Education in the Paint Industry for comment by the Council of the Association and a special meeting of the Council would be held in December to discuss not only the Report but also the draft Memorandum and Articles for the Incorporation of the Association and a document of future policy which had been circulated by the Honorary Officers. The Exhibition held in London in March had proved to be very successful indeed and the Exhibition Committee had already allocated a larger floor area for the 1962 Exhibition than for any previous Exhibition. A welcome sign was the participation by overseas companies either directly or through English associates.

At this stage, the President called upon the company to drink a toast to Mr. A. J. Gibson, a Past President, now in his eighty-fifth year, and he mentioned also the honour conferred on another Past President, Dr. L. A. Jordan, who was to deliver the Mattiello Lecture in the United States later that month.

The President then turned to the publication of the first of the Paint Technology

Manuals (*Non-convertible Coatings*) which had appeared at the end of April and the sales of which had been most encouraging. The second Volume (*Solvents, Oils, Resins and Driers*) was scheduled to appear at the end of October and it was hoped that the remaining Volumes would be appearing at six-monthly intervals. He knew that the company fully appreciated that none of the Volumes would have been published but for the untiring efforts of the Editors-in-Chief, C. J. A. Taylor and S. Marks. Both these members had devoted hours to the editing of the manuscripts and suggesting countless additions and amendments to the authors. The Association would forever be in their debt. It was, therefore, with very great pleasure that he was able to make a presentation of a gold watch to Mr. Taylor and a Murphy transistor radio to Mr. Marks as signs of the Association's appreciation. Both Mr. Taylor and Mr. Marks made speeches in reply, expressing their pleasure at the appearance of the first of the volumes, on which the original work began in 1954, and looking forward to the publication of the remainder of the volumes.

Dr. Newton Friend, the Senior Past President, expressed the thanks of the company to the Council for arranging the Reunion Dinner and Dr. L. A. Jordan also addressed the company. After these speeches Mr. I. C. R. Bews (Honorary Editor) showed slides made from colour transparencies which he had taken on his visit to the British Trade Fair in Moscow and this was followed by a considerable number of questions.

Before dispersing, those present signed cards to send to those Past Presidents and Past Honorary Officers unable to attend. This was the third occasion on which the Dinner had been held at the Wax Chandlers' Hall and it is now clear that it has become a permanent fixture in the Association's calendar.

Association Dinner-Dance, 1962

At the beginning of the New Year members of the Association will receive the form of application for tickets for the Association's biennial Dinner and Dance, which will take place at the Savoy Hotel, London, W.C.2, on Friday, 23 March, 1962. Sydney Jerome and his Orchestra will provide the music for dancing, and

after an interval for light refreshments there will be a cabaret.

The price of single tickets will be £3 3s. each, and members are requested not to apply for tickets before receiving their forms. However, non-members wishing to

receive application forms should write, as soon as possible, to the General Secretary of the Association at the address shown on the front cover of the *Journal*, so that the forms can be despatched to them at the same time as to members.

Bristol Section



The photograph shows (from left to right): MR. R. H. HAMBLIN, MR. F. J. KENNEDY, MR. F. ARMITAGE, MR. W. G. TAYLOR, MR. A. AITKENHEAD, MR. R. C. SOMERVILLE and MR. R. D. O'CONNOR.

FORMATION OF THE IRISH BRANCH

On 22 September the inaugural meeting of the Irish Branch of the Bristol Section took place at Jury's Hotel, Dublin, in the presence of thirty members and visitors. Mr. A. Aitkenhead, the Chairman of the Bristol Section, opened the proceedings by congratulating the Branch upon its formation and called upon Mr. R. C. Somerville, the Chairman of the Steering Committee, appointed at the exploratory meeting held in Dublin on 10 April, 1961, to report on the present position. Mr. Somerville stated that the Council had accepted the resolution

passed by the meeting for the inauguration of the branch and that the strength of the Branch at that date stood at eighteen members with applications from other candidates at present being considered by the Council. Three meetings had been arranged by the Steering Committee for the forthcoming month and it was hoped to hold further meetings each month before the first Annual General Meeting in April 1962. It would be necessary for the rules of the branch to be adopted by the members as soon as possible and it was expected that this would be circulated to all of the mem-

bers before the Extraordinary General Meeting to be held on the same evening as the October meeting.

The election of Honorary Officers of the Branch was confirmed as follows:

Chairman .. Mr. R. C. Somerville
 Honorary Secretary .. Mr. F. J. Kennedy
 Honorary Treasurer .. Mr. W. G. Taylor
 Honorary Publications Secretary .. Mr. R. D. O'Connor

At this point in the proceedings Mr. Aitkenhead congratulated Mr. Somerville on becoming the first Chairman of the Branch and asked him to take the chair for the remainder of the evening. The following

Committee members were duly elected:—

Mr. T. C. Byrne Dr. D. T. Long
 Mr. J. R. Darwin Mr. J. Ward

Following the election of the Honorary Officers and the Committee the General Secretary of the Association (Mr. R. H. Hamblin) gave a short talk on the past history and present position of the Association.

The meeting was then addressed by Mr. F. Armitage on "Future Trends in the Paint Industry" and in the ensuing discussion the following took part: Messrs. Brunt, Sharp, W. G. Taylor, R. D. O'Connor, S. Hughes and Dr. D. T. Long.

A vote of thanks to Mr. Armitage was proposed by Mr. R. D. O'Connor, seconded by Dr. D. T. Long and carried with acclamation.

London Section

JUNIOR GROUP PROGRAMME FOR 1961-2

Monday, 6 November

Works visit to the Ford Motor Company at Dagenham at 1.30 p.m. Any member of the London Section wishing to attend should apply to Mr. M. R. Mills, Milling Group Development Laboratories, British Oil & Cake Mills Ltd., Albion Wharf, Erith, Kent.

Thursday, 4 January

Lecture on Polymers by Mr. A. R. H. Tawn (preceded by a short Annual General Meeting).

Tuesday, 27 March

"Complaints on a New Wavelength", by D. E. Roe.

Tuesday, 17 April

Visit to Paint Research Station.

The lectures will be held in the Memorial Hall, Farringdon Street, London, E.C.4, at 7 p.m.

Manchester Section

VISIT TO GRANADA TV STUDIOS

On Friday, 22 September, 1961, a party of thirty members visited the Granada TV Studios, Manchester. The tour included many aspects of the production of television programmes and they saw the construction of sets, outside broadcast equipment, make up, etc. Three studios were visited where sets, cameras, equipment and technique were studied. Of particular interest were the sets for "Coronation Street" and members were able to record that they had actually been in some of the premises. On the more technical aspects

of production, the visit included control rooms, the equipment for playing back recorded features on tape and for showing films. Mr. H. Smith (Chairman) thanked the Company for a most interesting and informative afternoon—even if some of the illusions created on the screen had been shattered in the process.

Afterwards, many of the party proceeded to the West Towers Country Club, Marple, where the evening was spent in enjoying dinner and other convivial activities.

H. R. T.

Register of Members

The following elections to membership have been approved by the Council. The Sections to which the new members have been attached are given in italics.

Ordinary Members

- BURGOS, ENRIQUE REVILLA, Epalza 7-4, Bilbao, Spain. (*Overseas*)
- CANT, BRIAN REID, Sidney Cooke (Printing Inks) P/L, 3 Millars Road, Brooklyn, Victoria, Australia. (*Victorian*)
- HARTSHORN, GUY PONSONBY, M.A., British Titan Products Co. Ltd., Billingham, Co. Durham. (*Newcastle*)
- HILLS, BRIAN ANDREW, M.A., A.R.I.C., 50 Kinross Street, Blockhouse Bay, Avondale, Auckland, New Zealand. (*Auckland*)
- KRIKLER, MIGUEL, CHEM.ENG., Av. Bolivia 554-1, Lima, Peru, South America. (*Overseas*)
- LOWE, ARTHUR, M.SC., PH.D., 35 Darley Avenue, West Didsbury, Manchester, 20. (*Manchester*)
- MORELLE, MICHAEL RICHARD, B.A., 18 Watercroft Road, Halstead, Sevenoaks, Kent. (*London*)
- O'CONNOR, DANIEL JOHN, M.SC., PH.D., Taubmans Industries Ltd., Mary Street, St. Peters, New South Wales, Australia. (*New South Wales*)
- PLUNKETT, JOHN JOSEPH, 6 Pine Copse Road, Dundrum, Dublin, 14, Eire. (*Bristol*)
- RYAN, ANTHONY JOSEPH, B.SC., c/o Industrial Chemical Products P/L., 78 Princes Highway, St. Peters, New South Wales. (*New South Wales*)
- SMITHSON, JOHN MICHAEL, M.A., 26 Kingsley Drive, Adel, Leeds, 16. (*West Riding*)
- THOMSON, CULLEN WILLIAM, B.SC., Fletcher Industries Ltd., P.O. Box No. 67, Dunedin, New Zealand. (*Wellington*)

Associate Members

- BEAUMONT, GEOFFREY, 306 Meltham Road, Netherton, Huddersfield. (*West Riding*)
- BRYAN, WILLIAM, Balm Paints (N.Z.) Ltd., P.O. Box 1009, Auckland, C.1, Auckland, New Zealand. (*Auckland*)
- BURRELL, LESLIE GEORGE, 2 Cherry Close, Elmore, Lee-on-Solent, Hants. (*London*)
- CREAGH, PETER JOHN, A. C. Hatrick Pty. Ltd., Stephen Road, Botany, New South Wales, Australia. (*New South Wales*)
- DERBYSHIRE, CYRIL PETER, 11 Staines Avenue, Papatoetoe, Auckland, New Zealand. (*Auckland*)
- DESMARCHELIER, MICHAEL, c/o Geigy (Australasia) P/L., Hale Street, Botany, New South Wales, Australia. (*New South Wales*)
- FROST, KEITH WELLER, 104 Arcadia Avenue, Gympsea Bay, New South Wales, Australia. (*New South Wales*)
- HEYWOOD, DONALD BAY, 15 Grandview Drive, Campbelltown, New South Wales, Australia. (*New South Wales*)
- JACKMAN, RICHARD KEVIN, Henry H. York & Co. Pty. Ltd., 2 Harwood Place, Perth, Western Australia. (*South Australian*)
- JONES, DEREK FREDERICK ARTHUR, Western Ink Co., Paulton, Nr. Bristol, Somerset. (*Bristol*)
- LAMBERT, GRAEME ROSS, 34 Alto Street, Wentworthville, New South Wales, Australia. (*New South Wales*)

MILLTON, STEPHEN EDWARD, Atlantic Union Oil Co. (N.Z.) Ltd., P.O. Box 1059, Auckland, New Zealand. *(Auckland)*

NOWERS, MARTIN JOHN, 191 Selsdon Park Road, Addington, Surrey. *(London)*

SHARP, FRANK DAVID HIRST, "Culbin", Church Road, Dundonald, Co. Down, Eire. *(Bristol)*

THOST, PAUL OTTO ROBERT, General Motors-Holden Pty. Ltd., Box 4239, G.P.O., Sydney, New South Wales, Australia. *(New South Wales)*

Junior Member

MCLEOD, KEVIN WILLIAM, 92 Windsor Road, Northmead, New South Wales, Australia. *(New South Wales)*

Obituary

EDWARD L. TWEEDIE

We regret to record the death on 17 September, after a short illness, of Mr. E. L. Tweedie. He was an original member of the Manchester Section, and had been

one of its auditors for over 25 years. He was on the staff of Cornbrook Chemical Company Limited, Stockport, and was within a few months of completing 50 years' service with that Company. He leaves a widow and a daughter.

STUDENTS' COMPETITION

An International Students' Competition for an original paper on any subject allied to the art and science of metal finishing is being organised by the North West Branch of the Institute of Metal Finishing. Judges will take into consideration: Presentation, Age, Education and Training, Originality, Clarity of Statement and the Importance of Subject in relation to present Metal Finishing Technique. Further details and entry forms may be obtained from the Hon. Secretary, Mr. F. Spicer, "Suffield Cottage", Moorhead, Gildersome, Nr. Leeds.

arrangements will in due course be made to extend the scheme for other candidates.

NEWS OF MEMBERS



H. LAVELL

JOINT I.R.I./P.I. EXAMINATIONS

In view of the increasing number of candidates entering for the qualifying examinations at Associateship level in both rubber and plastics technology at the same stage of their careers, the Councils of the Plastics Institute and of the Institution of the Rubber Industry have agreed to recognise common ground in their courses and examination papers and have appointed a Joint Examining Board. The authority to award any qualification still, however, rests with the body in question. So far the scheme applies only to the so-called "chemistry route", but

Mr. H. Lavell, an Ordinary Member attached to the London Section, has been appointed to the Board of Directors of Industrial Colours Ltd.

PERKIN CENTENARY TRUST AWARDS

The trustees invite applications for the following awards which should be made on forms available from the Secretary of the Trust and must be received not later than 1 May, 1962.

The Perkin Centenary Fellowship

This award is offered for one or two years for the purpose of higher study of any subject approved by the Trustees. Candidates will be required to show *either* that they have had experience in an industrial firm or other institution concerned in the manufacture or the application of colouring matters, *or* that their intended field of study has a direct bearing on these subjects. The value of the Fellowship is £750 per annum with an additional grant of up to £100 per annum towards certain designated expenses. It may be tenable, from October 1962, at any university, technical college or other institution approved by the Trustees.

The Perkin Centenary Scholarship

Two such awards are offered, each for two years, renewable at the discretion of the Trustees for one further year, to enable candidates employed in an industrial firm or other institution concerned with the manufacture or the application of colouring matters to receive an education at a university or technical college. Each award will have a value of £350 per annum. This may be increased, at the discretion of the Trustees, to £400 per annum if the candidate appointed is required to live away from his normal place of residence. There is no means test and a successful candidate is not debarred from receiving the whole or a part of his normal salary from his employers during his tenure of the Scholarship.

Enquiries relating to these awards should be addressed to The Secretary, The Perkin Centenary Trust, c/o The Chemical Society, Burlington House, London, W.1.

RECENT BRITISH STANDARDS

The following British Standards have recently been issued:

B.S. 634 : 1961—Air-drying Insulating Finishing Varnish for Electrical Purposes.

This publication has been prepared under the supervision of the Electrical Industry Standards Committee, on which the Association is represented by Mr. L. Massey. Copies of the Standard may be obtained from the British Standards Institution, 2 Park Street, London, W.1, price 4s.

B.S. 217 : 1961—Red Lead for paints and jointing compounds.

The revision has resulted mainly in the fixing of an upper limit for the content of ordinary red lead for paints, and the raising of the minimum content of the non-setting variety.

The standard specifies materials, composition, non-setting properties, residue on sieve, oil absorption, value, colour matter soluble in water, and matter volatile at 100°C. Sampling methods of testing are also described.

Copies of this standard may be obtained at British Standards Institution Sales Branch, 2 Park Street, London, W.1, price 5/- each. (Postage will be charged extra to non-subscribers).

Forthcoming Events

(Note: Details are given of meetings arranged in the U.K. up to the 15th of the month following publication, and in South Africa and the Commonwealth up to the 15th of the second month after publication.)

Thursday, 2 November

Newcastle Section. A paper on metal finishing (title to be decided), by R. M. C. Logan, at the Royal Turks Head Hotel, Newcastle upon Tyne, at 6.30 p.m.

Friday, 3 November

Newcastle Section Junior Group. "Formulation", by K. F. Baxter, in the Rutherford College of Technology, Northumberland Road, Newcastle upon Tyne, at 3 p.m.

Monday, 6 November

Hull Section. Details to be announced.

London Section Junior Group. Works visit to the Ford Motor Company at Dagenham, at 1.30 p.m.

Thursday, 9 November

Technical Education Committee meeting at Wax Chandlers' Hall, Gresham Street, London, E.C.2, at 2.30 p.m.

New South Wales. "Thermosetting Acrylics", by Dr. B. James, in the Theatre, M.C.L. Building, Miller Street, North Sydney, at 6.15 p.m.

London Section. "Applications of Microwave Spectroscopy", by R. S. Tebble, B.Sc., Ph.D., F.INST.P. (Department of Physics, Sheffield University), in the Lecture Theatre, Royal Society of Tropical Medicine and Hygiene, Manson House, 26 Portland Place, London, W.1, at 7 p.m.

Scottish Section. "Solvent Selection for Modern Finishes", by J. E. Loible, in the Grand Hotel, Charing Cross, Glasgow, at 7.30 p.m.

Friday, 10 November

Manchester Section. "Television—A Persuasive Medium", by J. P. Phoenix, M.I.P.R., to be given at the Liverpool Constitutional Club, Tithebarn Street, Liverpool, at 6.30 p.m.

Monday, 13 November

Victorian Section. "Some Recent Developments in Latex Paints", by B. McGuinness, Jordan National Pty. Ltd.

London Section, Southern Branch. "The Testing of Ferrous Metals for Corrosion Resistance, by K. A. Chandler (B.I.S.R.A.), at the Polygon Hotel, Southampton, at 7.30 p.m.

Tuesday, 14 November

West Riding Section. "Advertising to and by Paint Firms", by N. R. Fisk, at the Hotel Metropole, Leeds, at 7.30 p.m.

Friday, 17 November

Association Council Meeting at Wax Chandlers' Hall, Gresham Street, London, E.C.2, at 11.30 a.m.

London Section. Ladies' Night at the Criterion Restaurant, Piccadilly, W.1.

Midlands Section. "Recent Developments in Polymeric Materials", by J. E. Stuckey, B.Sc., A.R.I.C., at Regent House, St. Philips Place, Colmore Row, Birmingham, at 6.30 p.m.

Saturday, 18 November

Scottish Section Student Group. "Some Recent Developments in the Technology of Drying Oils", by G. H. Hutchinson, A.R.I.C., at More's Hotel, India Street, Glasgow, C.2, at 10 a.m.

Tuesday, 21 November

Manchester Section. Joint Meeting with the Society of the Chemical Industry (Oils and Fats Group). Lecture entitled "Some Developments in Applied Oleo-Chemistry", by M. Josephs, B.Sc., Ph.D., A.R.I.C., to be given at the Manchester Literary and Philosophical Society, 36 George Street, Manchester, at 6.30 p.m.

Wednesday, 22 November

Western Australian Branch. Programme to be announced.

Friday, 24 November

West Riding Section. Annual Dinner and Dance at the Granby Hotel, Harrogate.

Bristol Section. "Wood Preservation", by R. Cockroft, A.I.W.Sc. (Forest Products Research Laboratory), at the Royal Hotel, College Green, Bristol, 1, at 7.15 p.m.

Bristol Section, Irish Branch. "Thixotropic Alkyds", by a representative of Cray Valley Products Ltd., together with a new colour film on the subject, at Jury's Hotel, Dublin, at 8 p.m.

Friday, 1 December

Midlands Section. Ladies' Evening at the George Hotel, Solihull.

Newcastle Section Junior Lecture. "Decorative Paints", by Dr. A. J. Seavell, in the Rutherford College of Technology, Northumberland Road, Newcastle upon Tyne, at 3 p.m.

Monday, 4 December

Bristol Section. Annual Dance at the Arnos Court County Club, Bristol.

Hull Section. "The Alkali Fusion of Fatty Acids", by Professor Weedon. Joint meeting with Oils and Fats Group of the S.C.I. and Hull Section of the R.I.C., at the Royal Station Hotel, Hull, at 7.15 p.m.

Wednesday, 6 December

Victorian Section. Annual Dinner, Melbourne University Union, Main Buffet. Guest speaker to be announced.

Thursday, 7 December

New South Wales Section. Annual Dinner at the "Amory".

London Section. "Aircraft Paints", by A. Macmaster, M.Sc., A.R.I.C. (Ministry of Aviation), in the Lecture Theatre, Royal Society of Tropical Medicine and Hygiene, Manson House, 26 Portland Place, London, W.1, at 7 p.m.

Newcastle Section. A paper on driers (title to be announced later), by C. T. Morley-Smith, at the Royal Turks Head Hotel, Newcastle upon Tyne, at 6.30 p.m.

Bristol Section. "Paint Progress—A Myth?". Joint meeting with Birmingham Paint, Varnish and Lacquer Club in Birmingham at the Imperial Hotel, at 6.30 p.m.

Association Council Meeting at Wax Chandlers' Hall, Gresham Street, London, E.C.2, at 11.30 a.m.

Friday, 8 December

Manchester Section. "Architectural Approach to Colour in Building", by A. E. Hurst, F.I.B.D., to be given at the Manchester Literary and Philosophical Society, 36 George Street, Manchester, at 6.30 p.m.

Monday, 11 December

London Branch, Southern Branch. "The Interaction of the Pigment with the Medium," by Dr. V. T. Crowl (Paint Research Station), at the Royal Beach Hotel, Southsea, at 7.30 p.m.

Thursday, 14 December

Scottish Section. "Wines, Tasting and Testing", by H. F. Barnes, in the Grand Hotel, Charing Cross, Glasgow, at 7.30 p.m.

Friday, 15 December

Bristol Section. A paper to be given by I. C. R. Bews, B.Sc., A.R.I.C.

Saturday, 16 December

Scottish Section Student Group. A Film Show at More's Hotel, 18 India Street, Glasgow, C.2, at 10 a.m.

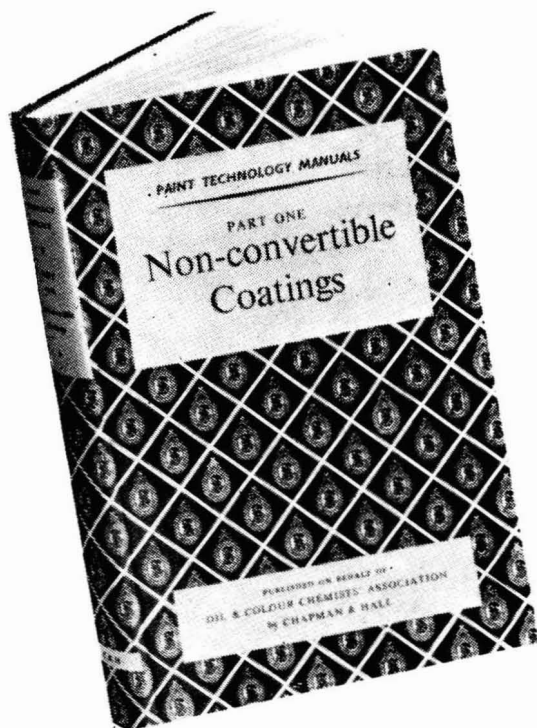
Wednesday, 27 December

Western Australian Branch. Dinner and Golf Day.

PAINT TECHNOLOGY MANUALS

Editors-in-Chief :

C. J. A. Taylor, M.Sc., A.R.I.C. and S. Marks, M.Sc.(TECH.), F.R.I.C.



Collator :

J. B. G. Lewin, B.Sc., F.R.I.C.

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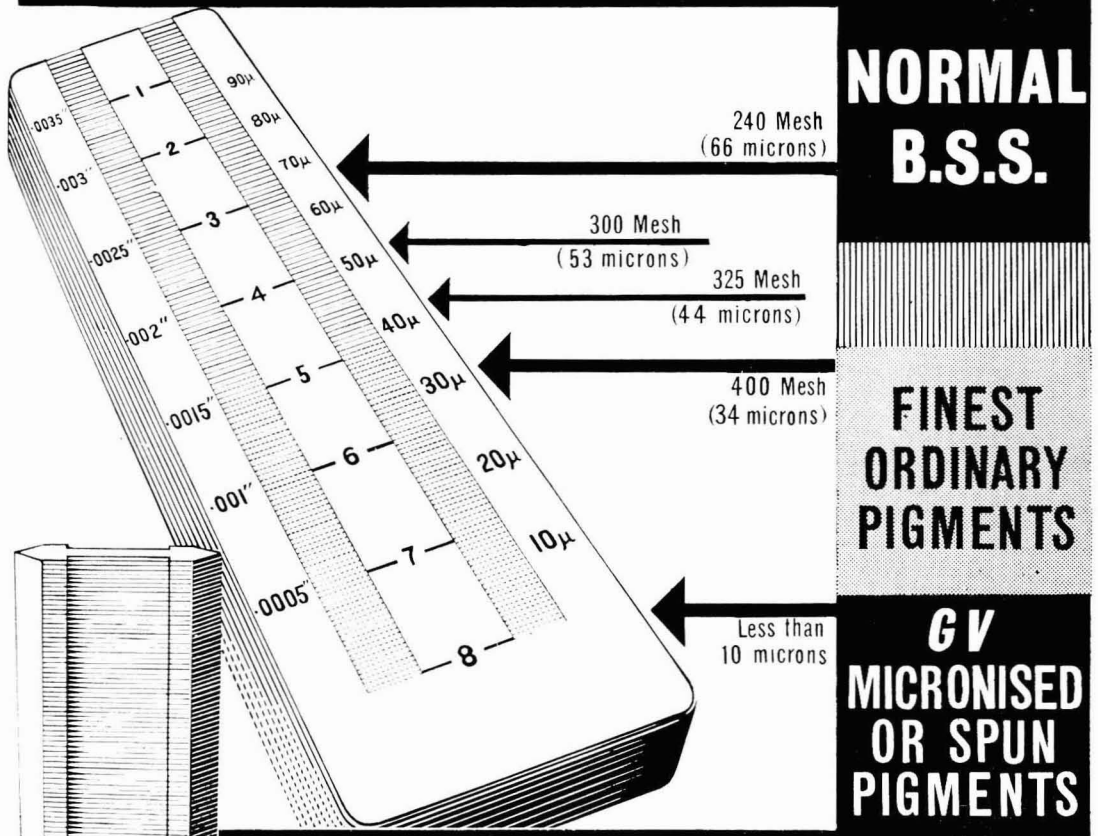
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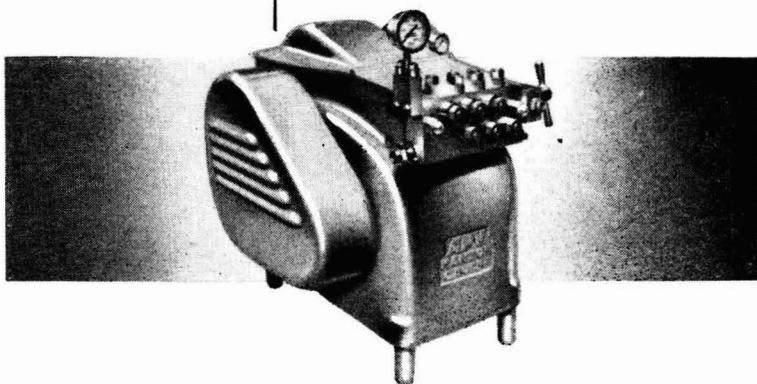
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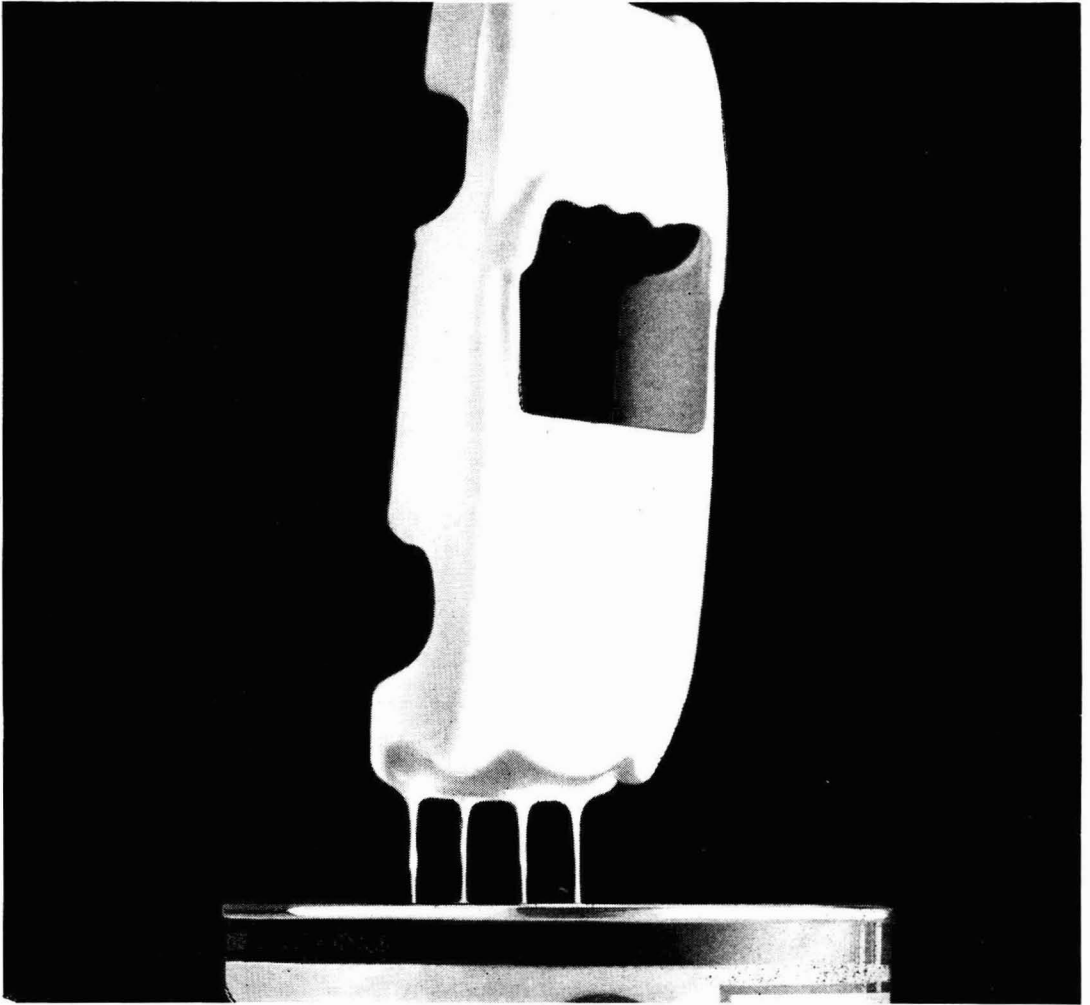


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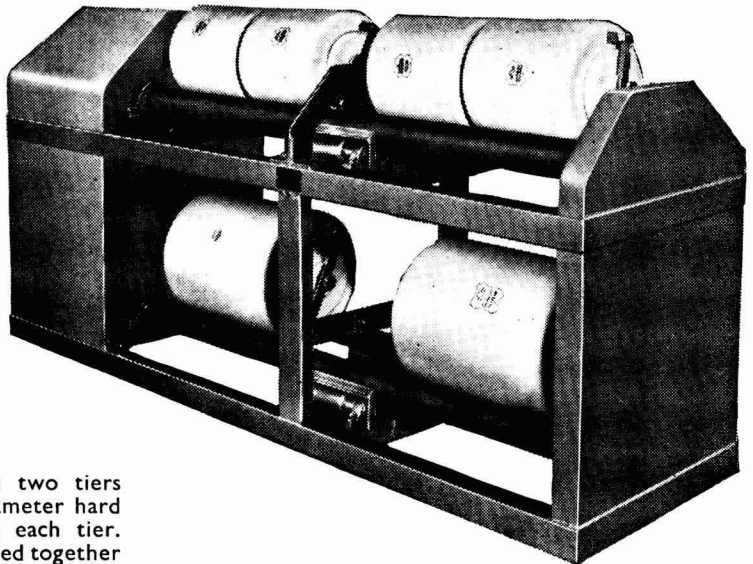
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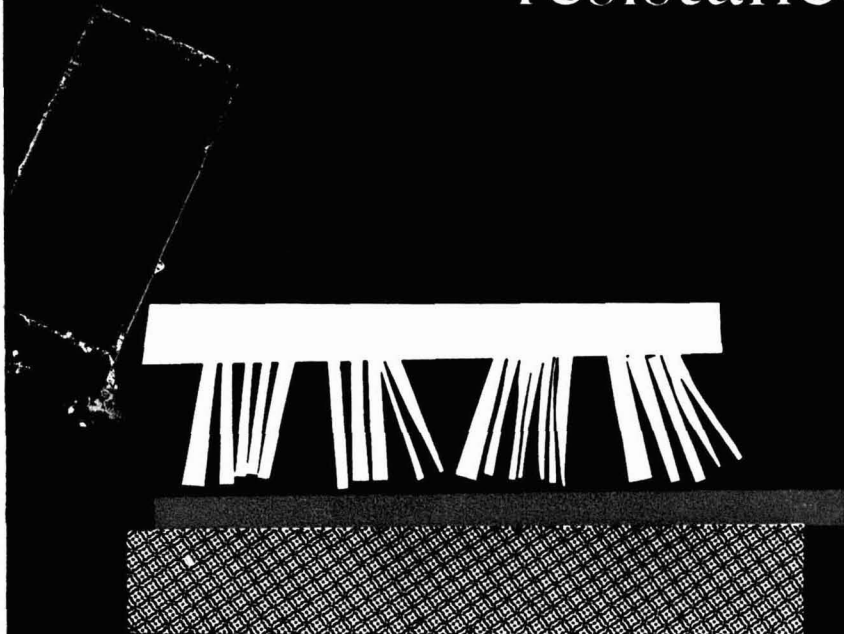
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