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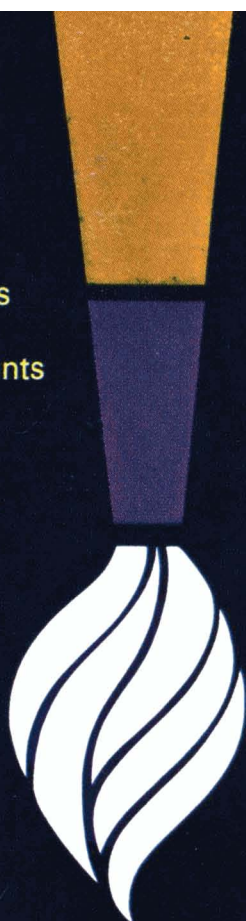
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Transactions and Communications

Water absorption of phenolic varnish films

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Summary

Accurate values for the amount of water absorbed by unpigmented oil-phenolic varnishes are only obtained when the films are subjected to at least five absorption-desorption cycles. Solvent trapped in the film is thus gradually released and the absorption values become constant.

The varnishes studied do not show hysteresis in their isothermal sorption curves. It is expected that similar types of material will exhibit the same behaviour. The complete stepwise procedure does not, therefore, appear necessary in characterising the absorption properties of clear varnishes. Adequate information is obtained with several successive exposures to zero and 99 per cent RH. Rapid-drying materials require one or two more cycles to remove trapped solvent. The values thus obtained with paraphenylphenolic varnishes are related to their exterior durability on wood.

Keywords

Properties, characteristics and conditions primarily associated with dried or cured films

water absorption

Types and classes of coating

phenolic varnish

L'absorption d'eau des feuils de vernis phénolique

Résumé

On peut obtenir des valeurs exactes de la quantité de l'eau absorbée par des feuils de vernis phénoliques modifiés pas huile et non pigmentés, seulement dans le cas où les feuils sont subis à cinq cycles d'absorption-désorption. En cette manière le solvant retenu dans le feuil est libéré graduellement et les valeurs d'absorption deviennent constantes.

Les vernis que l'on a étudiés ne démontre pas d'hystérésis dans leurs courbes de sorption isothermales. On attend que les types de matière semblables démontrent le même comportement. Ainsi il ne paraît pas nécessaire de caractériser les propriétés d'absorption des vernis clairs. On obtient de l'information suffisante par plusieurs expositions successives aux humidités relatives de zéro et de 99 pour cent. Les vernis qui sèchent rapidement exigent un ou deux cycles de plus pour enlever le solvant attrapé. Les valeurs si-obtenues à partir des vernis à base de paraphénylphénol sont liées à leur durabilité à l'extérieure sur bois.

Wasserabsorption von Phenolharzlackfilmen

Zusammenfassung

Man kann nur dann genaue Werte für die von unpigmentierten Phenolharzlacken auf Ölbasis aufgenommene Menge Wasser erhalten, wenn der Film zumindest fünf Absorptions-Desorptionszyklen unterworfen wurde. Auf diese Weise wird im Film zurückgehaltenes Lösungsmittel allmählich entfernt, und die Absorptionswerte werden konstant.

Die untersuchten Lacke zeigen in ihren isothermen Sorptionskurven keine Hysterese. Es ist anzunehmen, dass Stoffe ähnlicher Art sich ebenso verhalten. Daher scheint die vollständige stufenweise vorzunehmende Prozedur zur Charakterisierung der Absorptionseigenschaften von Klarlacken unnötig zu sein. Mit mehreren sukzessiven Exponierungen bei 0 und 99%

relativer Luftfeuchtigkeit erhält man ausreichende Information. Sehr rasch trocknende Erzeugnisse erfordern 1 oder 2 zusätzliche Zyklen, um zurückbehaltenes Lösungsmittel zu entfernen. Die so mit Paraphenylphenolharzlacken erhaltenen Werte stehen mit ihrer Wetterbeständigkeit auf Holz in Beziehung.

Поглощение воды феноловыми лаковыми пленками

Резюме

Точные количества воды поглощенной непигментированными масляно-феноловыми лаками могут быть определены лишь в том случае если пленки подвергаются по крайней мере пяти циклам абсорбции и десорбции. Растворитель улавливаемый в пленке таким образом постепенно выделяется и значения абсорбции становятся постоянными.

Изученные лаки не проявляют гистерезиса на изотермических кривых сорбции. Можно ожидать что сходные типы материалов проявят аналогичное поведение. Полный ступенчатый ход процесса поэтому не оказывается обязательно необходимым для характеризации абсорбционных свойств прозрачных лаков. Получены соответствующие данные для ряда последующих выдержек при ноль процентах и 99-ти процентах относительной влажности. Быстро высыхаемые материалы требуют один или два добавочных цикла для устранения улавливаемого растворителя. Величины полученные таким образом с парафенилфенольными лаками отнесены к их наружной устойчивости на дереве.

Introduction

Water absorption has long been considered an important property of coatings subjected to exterior exposure because water, in the form of rain or high humidity, is one of the chief elements of weather. When wood is the substrate, there is the added possibility that moisture will reach the back of the film owing to the permeability of wood to water. Many studies have therefore been made to attempt to relate the water absorption properties of coatings with their exterior durability on wood.

Measurements of this property have traditionally been made by immersing free films in water, withdrawing them at intervals, and weighing them after removing surface water by blotting. This procedure is adequate for pigmented coatings, which absorb considerable quantities of water. Browne, of the US Forest Products Laboratory, carried out extensive work in this field[1].

The immersion method is not applicable to clear coatings because the amount of water absorbed is small. It is frequently less than the quantity of water-soluble material present in the film, so that zero or negative values for water absorption can be obtained. When positive values are found, the weight of water absorbed by films of the usual sample size is often close to the error of the normal analytical balance. The blotting procedure and losses due to evaporation during weighing also contribute to the inaccuracy of the method. Hence, results have not been useful in attempts to establish a relation between water absorption and the durability of clear coatings for exterior wood[2].

For several years the quartz-spring balance of McBain and Bakr[3] has been used in the materials laboratories of the Division of Building Research, National Research Council of Canada, for measuring the water absorption-desorption properties of inorganic building materials. With precise temperature control of both the water bath in which the sample tube is immersed and the separate bath for the water vapour source, it is possible to determine with a high degree of accuracy the quantity of water absorbed by a material at any given relative

humidity. As the sample is not immersed in liquid water, soluble products are not lost in this procedure.

Because of the difficulties with the immersion method and the satisfactory results obtained with inorganic materials using the spring balance-water vapour procedure, the latter was applied in determining the water absorption properties of oil/phenolic resin varnishes. This paper reports the results obtained with these materials and the precautions necessary when the procedure is used with organic coatings.

Materials and procedure

The paraphenylphenolic varnishes used in this study and the absorption-desorption apparatus have been described[1]. Further discussion of the procedure as used with inorganic powders is given by Feldman and Sereda[5]. The quartz bucket used for holding powders was replaced by a platinum loop to allow free access to both sides of free films. The latter were obtained from tin foil with three weeks' drying at 23 ± 2°C and 50 ± 2 per cent RH, both before and after removal of the film by amalgamation of the foil.

Each air-dried film was cut into four pieces, about 3in by ½in, and these were suspended from the platinum loop. The specimens were evacuated in the apparatus to constant weight (usually 48 to 72 hours) before being subjected to water absorption and desorption. The water source was first degassed to ensure that only water vapour was introduced into the sample tubes.

Preliminary tests were made to discover any differences in absorption and desorption properties between free films prepared from tin foil and those prepared from photographic paper. Films were equilibrated at various relative humidities, increasing from zero to nearly 99 per cent, and then desorbed stepwise. At the end of one or two cycles, it was found that the effect of film preparation was completely obscured by weight losses of the films. This was attributed to removal of trapped solvent during the absorption-desorption process[4].

It was, therefore, necessary to establish whether the solvent loss had an effect on water absorption and, if so, to determine how many cycles were required to eliminate it. In subsequent tests, the intermediate water vapour pressures were omitted. The films were alternately subjected only to zero and near 99 per cent RH until constant weight under the first conditions and constant water absorption under the second were obtained. Only then were films exposed to stepwise absorption and desorption to obtain the complete isothermal water sorption curves.

Results

Water absorption at saturation

As previously shown[4], several cycles were required to remove most of the solvent and oxidation products and to attain constant weight. The amount of water absorbed during each of the quick absorption-desorption cycles is given in Table 1. Again, it may be seen that at least five cycles are required before absorption values become fairly constant. This coincides with the number of cycles necessary to reach constant weight.

Table 1

*Water absorption values in each absorption-desorption cycle**

Water absorbed near 99% RH in per cent by weight of evacuated film

	15-gal Varnishes		20-gal Varnishes				30-gal Varnishes		40-gal Varnishes				
Cycle No.	1020 Tung	1021 Linseed	893 Tung	902 Linseed	1022 Soya	1024 DHC	894 Tung	903 Linseed	901 Tung	905 Linseed	1023 Soya	1025 DHC	Cycle mean
1	0.600	0.712	0.687	0.817	0.846	0.887	0.801	0.993	0.995	1.065	1.210	1.143	0.90
2	0.762	0.819	0.830	0.920	0.938	0.956	0.898	1.094	1.102	1.150	1.261	1.217	1.00
3	0.840	0.900	0.899	0.999	0.991	1.015	0.974	1.162	1.154	1.215	1.296	1.267	1.06
4	0.883	0.934	0.922	1.015	1.017	1.042	1.019	1.186	1.177	1.240	1.331	1.300	1.09
5	0.903	0.954	0.940	1.023	1.035	1.067	1.046	1.208	1.186	1.255	1.351	1.320	1.11
6	0.901	0.964	0.949	1.025	1.041	1.077	1.044	1.206	1.181	1.255	1.351	1.318	1.11
7	0.905	0.960	0.953	1.023	1.041	1.077	1.046	1.208	1.183	1.255	1.347	1.322	1.11

* Absorption values corrected for weight loss in previous desorption

Increases in water absorption during the middle cycle and weight losses at the end of the seventh cycle are given in Table 2. These values are plotted against each other in Fig. 1, together with the least squares regression curve for a linear relation between them. The correlation coefficient, where $r = 1$ is perfect correlation and $r = 0$ is no correlation at all, was calculated to be 0.894. This means that 80 per cent of the increase in water absorption can be ascribed to the loss in weight of the films. The intercept at zero weight loss is 0.072 per cent water absorption increase, indicating that another factor has some effect on the results. This might be related to ease of swelling as the number of cycles increases.

Table 2

*Weight loss and change in water absorption after seven cycles**

Per cent by weight of evacuated film

Oil type	Tung		Linseed		Soya		Dehyd. Castor	
	Wt L	Abs Ch	Wt L	Abs Ch	Wt L	Abs Ch	Wt L	Abs Ch
Oil content	15 gal (58.3% oil or 1:1.4 resin:oil)							
	0.418	0.305	0.319	0.248	—	—	—	—
	20 gallon (66.7% or 1:2)							
	0.455	0.266	0.285	0.206	0.218	0.195	0.222	0.190
	30 gallon (75% or 1:3)							
	0.307	0.245	0.259	0.215	—	—	—	—
	40 gallon (80% or 1:4)							
	0.251	0.188	0.240	0.190	0.215	0.137	0.208	0.179

Wt. L. = weight loss

Abs. Ch. = change in water absorption

* Absorption values corrected for weight loss in previous desorption
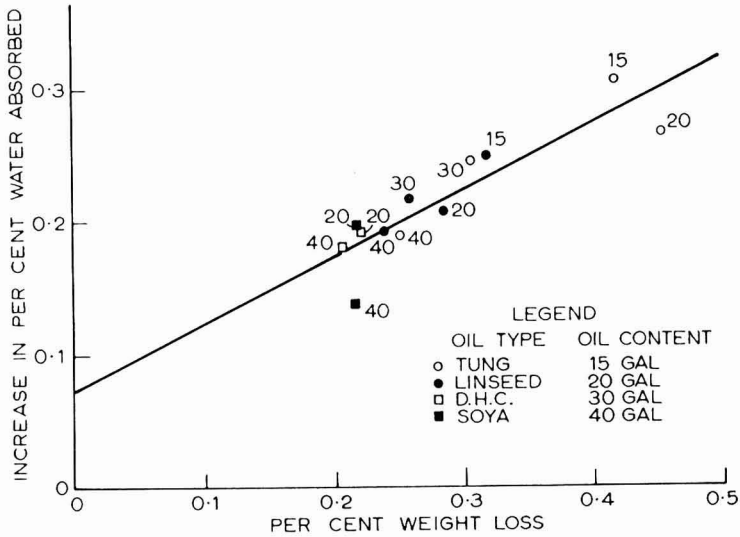
Fig. 1. Weight loss vs water absorption increase after seven cycles
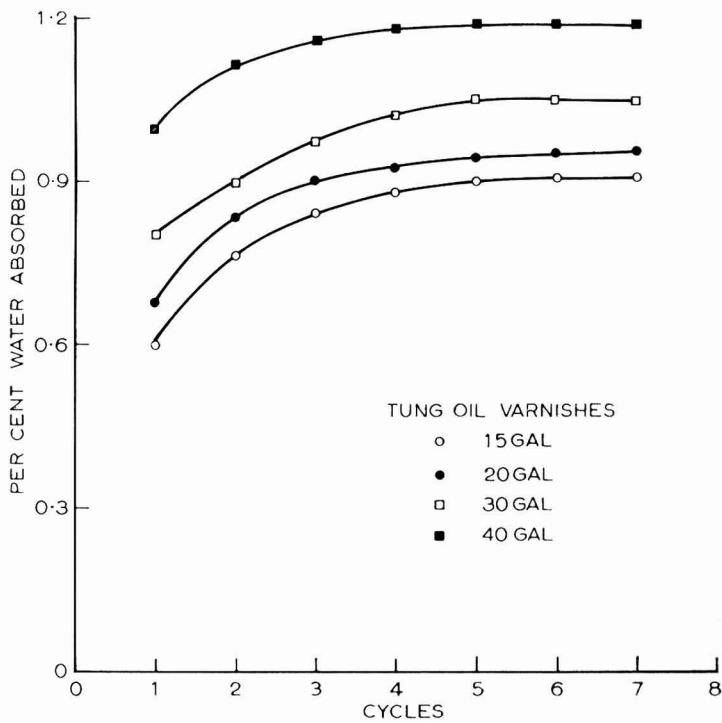
Fig. 2. Effect of oil content on water absorption

The results show that trapped solvent, which causes most of the weight losses, does interfere with water absorption of the films. It seriously affects the values obtained because the unpigmented films absorb so little water. For example, water absorption of the 20-gal tung varnish increased from 0.687 per cent in the first cycle to 0.953 per cent in the seventh. Although this increase is only 0.266 per cent of the film weight, it is 38.7 per cent of the first absorption value. The smallest increase was 11.3 per cent for the 40-gal soya varnish and the largest was 50.8 per cent for the 15-gal tung.

The effect of oil content on water absorption is shown in Fig. 2 for one oil. Fig. 3 illustrates the effect of oil type at 80 per cent (i.e., 40 gal) oil content. From the tables and figures it may be seen that the rapid-drying 15- and 20-gal tung varnishes exhibited the greatest changes in water absorption. The latter varnish changed less than the 15-gal one, although it lost more weight during the cycles because of its higher content of drier, which led to more entrapment of solvent. The largest part of the increases took place in the first cycle, after which the changes more nearly resembled those occurring in the majority of the varnishes. Increases in water absorption of the long-oil soya and castor varnishes
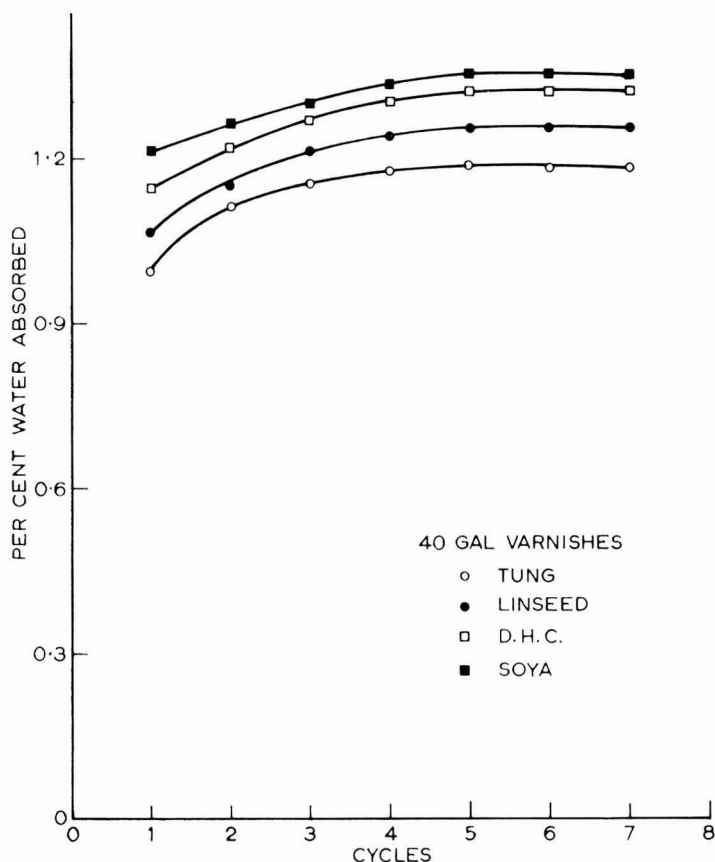
Fig. 3. Effect of oil type on water absorption

were more gradual, but five cycles were still needed before constant values were obtained.

When reproducible absorption results were established, it was found that they were related to composition of the varnish. Thus, with any one oil, the lower the oil content the lower the amount of water absorbed. Tung oil varnishes absorbed less water than the corresponding linseed and about the same as the next shorter linseed varnish. This correlates well with their exterior durability on red cedar, where the 40-gal tung approached the performance of the 30-gal linseed varnish and the 30-gal tung was rated equal to the 20-gal linseed[6]. Linseed varnishes absorbed less water than soya and dehydrated castor varnishes. These two oils behaved similarly, with soya absorbing less water at 20-gal length and DHC less at 40-gal.

Absorption-desorption isotherms

The amounts of water absorbed by the four 20-gal varnishes, with increasing and decreasing relative humidities, are given in Table 3. The curve for the tung varnish is plotted in Fig. 4 and that for DHC in Fig. 5. These varnishes showed the greatest difference in results. It may be seen that at the end there were still slight losses in weight even after the seven previous cycles. These occurred because the stepwise absorption-desorption cycle required about three months whilst the seven rapid cycles took only about one month. Again it is noted that the tung varnish had the largest weight loss, that linseed was intermediate, and that the other two had the least loss.

Weight losses are most probably due to traces of solvent, since there would be no oxidation in the absence of oxygen. It can be assumed that solvent loss would occur during desorption and not during absorption of water. It is also

Table 3
Per cent increase in weight of 20-gal varnishes at various relative humidities

	Absorption					Desorption			
Relative Humidity	893 Tung	902 Linseed	1022 Soya	1024 DHC	% RH	893 Tung	902 Linseed	1022 Soya	1024 DHC
8.0	0.090	0.085	0.100	0.095	96.0	0.925	1.005	1.015	1.055
19.0	0.175	0.185	0.200	0.190	93.0	0.880	0.955	0.975	1.010
32.0	0.275	0.300	0.325	0.315	88.0	0.805	0.900	0.920	0.950
47.5	0.400	0.450	0.450	0.460	82.5	0.730	0.835	0.850	0.875
59.5	0.520	0.585	0.580	0.590	79.5	0.690	0.790	0.810	0.835
70.0	0.625	0.685	0.680	0.705	71.5	0.595	0.695	0.705	0.740
76.0	0.680	0.760	0.760	0.770	62.5	0.490	0.600	0.600	0.635
80.5	0.730	0.800	0.810	0.825	53.5	0.400	0.490	0.495	0.535
84.0	0.775	0.840	0.850	0.875	44.0	0.310	0.385	0.400	0.420
87.0	—	0.875	0.885	0.915	35.5	0.225	0.310	0.330	0.335
89.0	0.840	0.905	0.920	0.945	30.0	0.175	0.250	0.270	0.275
94.5	0.905	0.965	0.980	1.010	21.0	0.085	0.150	0.175	0.180
97.0	0.945	1.010	1.015	1.050	12.5	0.001	0.070	0.100	0.095
99.0	0.975	1.040	1.050	1.085	7.5	−0.025	0.020	0.050	0.050
					0	−0.09 *	−0.05 *	−0.02 *	−0.025*

*Extrapolated Values
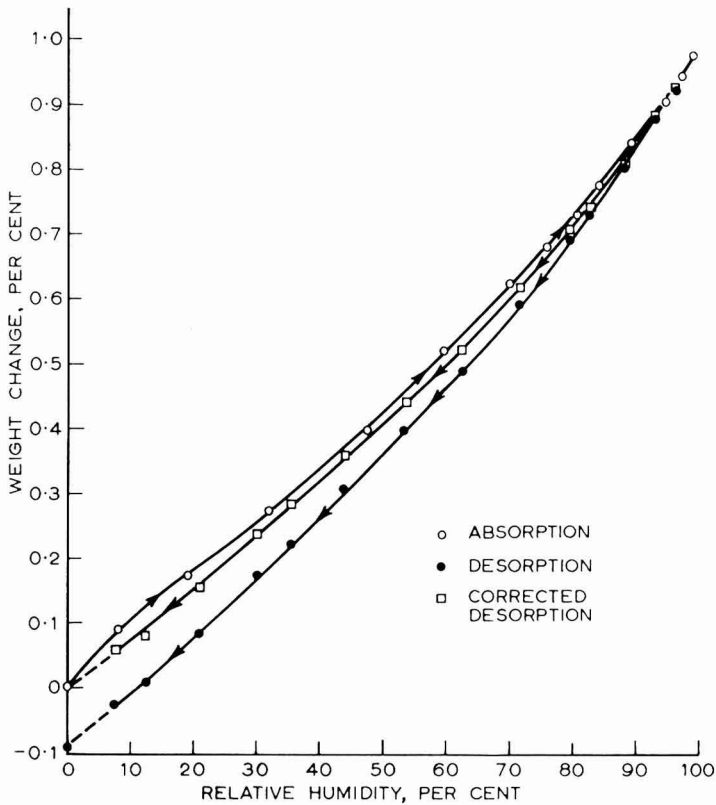
Fig. 4. Water sorption isotherm for 20-gal tung-phenolic varnish

probable that solvent would be lost fairly uniformly rather than at the beginning
or the end of desorption. Consequently, the desorption results can be corrected
for solvent loss by pro-rating the latter in proportion to the decrease in relative
humidity from 99 per cent. The corrected values are given in Table 4 and those
for tung and DHC varnishes are included in the respective figures.

The results show that there is little difference between absorption and desorp-
tion curves for oil/phenolic resin varnishes. At the beginning of the absorption
cycle the amount absorbed is slightly higher in proportion to relative humidity
than in the middle of the cycle. Otherwise, there are no distinguishing features
in the curves. This lack of hysteresis is in marked contrast to the situation with
porous inorganic materials such as concrete.

In comparing Tables 1 and 3, the increase in water absorbed at saturation
after stepwise absorption is, at the most, about 2.5 per cent of that observed
during the seventh rapid cycle. Part of the increase may be due to differences in
humidity, because no attempt was made to obtain exactly 99 per cent RH
during the short cycles. It appears that there is not sufficient information gained
from the complete stepwise procedure to justify the time required to carry it out.
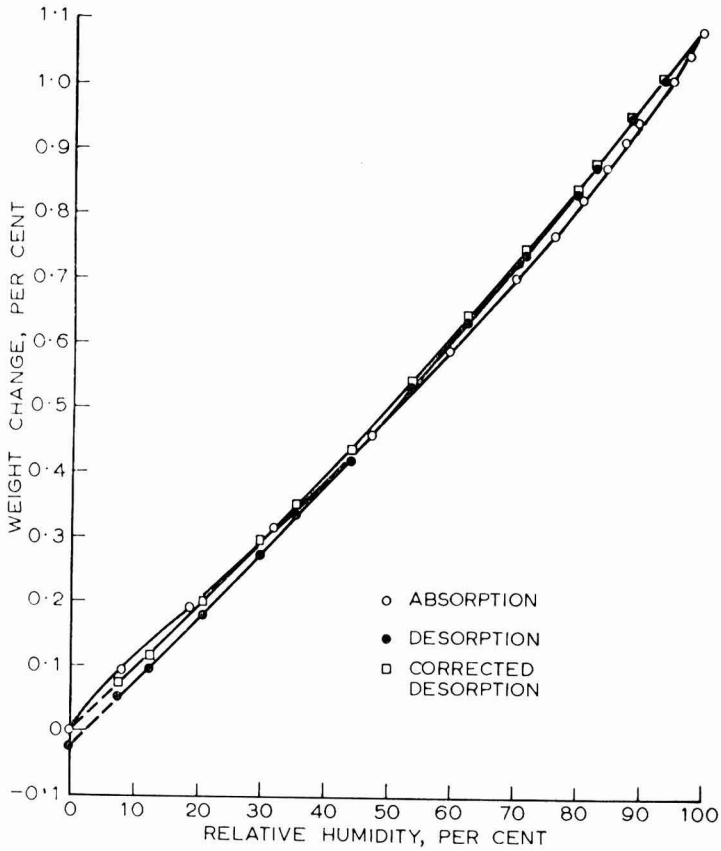
Fig. 5. Water sorption isotherm for 20-gal DH castor varnish

Table 4
Corrected desorption weights
Per cent by weight of evacuated weight

Relative humidity	893 Tung	902 Linseed	1022 Soya	1024 DHC
99.0	0.975	1.040	1.050	1.085
96.0	0.928	1.006	1.016	1.056
93.0	0.885	0.958	0.976	1.011
88.0	0.815	0.906	0.922	0.953
82.5	0.745	0.843	0.853	0.879
79.5	0.708	0.800	0.814	0.840
71.5	0.620	0.709	0.711	0.747
62.5	0.523	0.618	0.607	0.644
53.5	0.441	0.513	0.504	0.546
44.0	0.360	0.413	0.411	0.434
35.5	0.283	0.342	0.343	0.351
30.0	0.238	0.285	0.284	0.292
21.0	0.156	0.189	0.191	0.200
12.5	0.080	0.114	0.117	0.117
7.5	0.058	0.066	0.068	0.073
0	0	0	0	0

Discussion

As concluded in the previous paper[4], small amounts of solvent are trapped in oil/phenolic resin varnishes. This solvent interferes with water absorption and several cycles of absorption and desorption are required to remove it so that true absorption values can be obtained. Although first results may be indicative of freshly prepared films, the constant values give a truer picture of varnishes that have been wetted and dried during natural exposure.

Increase in water absorption is closely related to weight loss of the film. Under absorption-desorption conditions, water vapour gradually replaces most of the volatile matter in the film, resulting in an increase in water absorption. In exposure studies, such changes in absorption have usually been attributed to degradation caused by weathering. Increases of up to 50 per cent of the initial value can evidently be caused solely by loss of trapped solvent.

Final or constant absorption values are related to the components of the varnish. Those with the most phenolic resin absorb the least amount of water. Although tung varnishes exhibit the greatest increase in water absorption, because their rapid drying traps the most solvent, the final amount is less than for varnishes made with other oils at the same oil content. The low water absorption correlates well with their good exterior durability compared to other clear finishes on wood. This might be expected because water absorption is generally associated with swelling of the absorbing material[1]. Coatings that exhibit the lowest absorption are less subject to swelling and shrinkage forces during wetting and drying cycles. Consequently, they should be more durable. This is indeed the case with these clear finishes.

Because of the sensitivity of the spring balance, the water vapour method is more precise than the immersion method using an analytical balance. In immersion tests, the quantity absorbed is affected, not only by the swelling characteristics of the film, but also by its wettability by liquid water. In these studies, phenolic varnishes generally attained equilibrium within 48 hours at any given vapour pressure and absorption was almost linear to 75 per cent RH and increased gradually after that. These results indicate that the films do not swell very much in water. They are also hydrophobic, which retards water absorption. Finally, in immersion there are no absorption-desorption cycles, which have been shown necessary to remove strongly-held solvent. Consequently, the solvent remains in the film and seriously affects absorption results. Together with removal of water soluble oxidation products, this accounts for the extremely low water absorption values obtained with immersion tests on clear finishes.

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Paints for high-speed aircraft*

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Summary

In the aircraft industry, as in most industries, paint functions both as protection and decoration. Newer types of aeroplane, which are designed to operate at cruising speeds in or near the supersonic region, will encounter conditions which are often more severe than those that apply to the models in use today. Higher speeds will lead to higher skin temperatures, owing to a kinetic heating effect, and the paint system will have to withstand these temperatures and also resist the different types of operating fluids that will be necessary in aircraft operating at them. Further, high temperatures will cause boiling of condensed water in the fuselage, and this may cause severe corrosion if the coating system cannot resist it.

Possible types of coating system for interior and exterior surfaces under these conditions are discussed, as are the problems encountered with other allied materials, such as jointing compounds.

Another problem which is encountered is that of erosion of exterior coatings, for instance when flying through rain at high speeds. Methods of combating this effect are outlined.

Finally, the paper looks further into the future, when even higher speeds will engender body temperatures of up to 300°C, and shows the kinds of paint system which may be used.

Keywords

Types and classes of coating
aircraft coating
sealant

Peintures pour les avions de haute vitesse

Résumé

Dans l'industrie de l'aviation, comme dans la plupart des industries, la peinture s'emploie pour protéger et pour décorer également. Les nouveaux types d'avions qui sont conçus à opérer dans ou proche de la région supersonique, recontreront des conditions souvent plus sévères que celles qui font face aux modèles actuellement en service. Les vitesses plus élevées provoqueront des températures de coque plus élevées à cause de l'effet du chauffage kinétique, et le système de peinture devra résister ces températures et à la fois les types différents des liquides qui se trouveront aux avions destinés à opérer à ces températures élevées. D'ailleurs, les températures élevées provoqueront l'ébullition de l'eau condensée qui se trouve au fuselage, et qui produira de la corrosion sévère dans le cas où le système de peinture ne pourrait pas la résister.

On discute des types possibles des systèmes de revêtement pour les surfaces intérieures et extérieures également, sous des conditions mentionnées ci-dessus. D'ailleurs on discute les problèmes mis en évidence par des matières connexes, par exemple les compounds pour joints.

Un autre problème que l'on rencontre, c'est l'érosion des revêtements extérieures, qui se produit en volant à travers la pluie aux vitesses élevées. On mentionne des méthodes pour combattre cet effet.

Enfin, l'exposé lance un regard vers l'avenir plus lointain, où les vitesses même plus élevées provoqueront des températures de coque vers 300°C, et on suggère les types de systèmes de peintures que l'on pourrait utiliser.

*Presented to the Newcastle Section on 6 November 1969.

Lacke für Sehr Sehnell Fliegende Luftfahrzeuge

Zusammenfassung

In der Flugzeugindustrie dient, wie in jeder anderen Industrie, die Lackierung sowohl dem Schutze als auch dem Schmuck. Neuere Flugzeugmodelle, die dazu bestimmt sind bei Dauergeschwindigkeiten in oder nahe der Überschallregion zu kreuzen, werden Bedingungen ausgesetzt, welche oft schwerer sind als solche, die die gegenwärtig-gebrauchten Modelle aushalten müssen. Als Folge des kinetischen Erhitzungseffektes haben grössere Geschwindigkeiten höhere Hauttemperaturen zur Folge, und das Anstrichsystem muss diese Temperaturen aushalten. Letzteres muss ebenfalls beständig gegen die verschiedenen Arten von Flüssigkeiten sein, die für den Betrieb der untesrolchen Bedingungen fliegenden Flugzeugegebraucht werden. Hohe Temperaturen verursachen ausserdem Kochen des am Rumpfe kondensierten Wassers, und dies wiederum würde ernste Korrosion verursachen, wenn das Anstrichsysten dagagen nicht genügend widerstandsfähig ist.

Für die Anwendung an Innen- und Aussenflächen unter diesen Bedingungen brauchbare Typs von Anstrichsystemen werden ebenso besprochen, wie die Probleme, denen man bei anderen verwandten Materialien, z.B. Abdichtmitteln, begegnet.

Erosion der Aussenlackierung ist ein anderes vorkommendes Problem, z.B. beim Fliegen durch Regen mit grossen Geschwindigkeiten. Methoden zur Bekämpfung dieser Wirkung werden skizziert.

Schliesslich folgt ein Ausblick in die Zukunft, wenn sogar noch höhere Geschwindigkeiten Temperaturen des Flugzeugrumpfes von bis zu 300 C verursachen werden; darin werden auch die Arten von Anstrichsystemen erwähnt, welche verwendet werden könnten.

Краски для скоростных самолетов

Резюме

В авиационной промышленности, как и в других промышленностях, краска играет роль защиты и украшения. Новейшие типы самолетов, расчитанные для крейсерских сверхзвуковых или близких к ним скоростей, сталкиваются с более суровыми условиями чем условия которым подвержены самолеты применяемые в настоящее время. Большие скорости вызывают более высокие температуры обшивки в виду кинетического теплового эффекта, красочная система должна противостоять этим температурам и быть устойчивой против действия различных рабочих веществ, применяемых на самолетах при этих скоростях. Кроме того высокие температуры могут вызвать кипение конденсационной воды в фюзеляже, что в свою очередь приведет к значительной коррозии, если система покрытий не сможет ей противостоять.

Обсуждаются возможные типы покрытий для внутренних и внешних поверхностей при этих условиях и также проблемы связанные с другими сходными материалами, как например уплотняющие и сцепляющие соединения.

Добавочной проблемой является эрозия наружных покрытий, например в полетах при больших скоростях в дождливую погоду. Описываются методы для преодоления этого эффекта.

В заключение статья заглядывает в будущее при наличии еще больших скоростей, вызывающих температуры корпуса до 300°C и указывает виды красочных систем которые войдут в применение.

Introduction

Paints are widely used on aircraft for the protection of aluminium and other alloys against corrosion. They may also have other functions to perform, such as reflecting heat to reduce the temperature of the structure, camouflage, and marking.

High speed aircraft need to be painted for all the above reasons. For all current designs intended to operate at speeds up to Mach 2.5, the combination of metals involved is likely to be much the same as has been used for several

generations, predominantly aluminium, together with steel, titanium, magnesium etc. Faster aircraft are likely to use other materials, such as stainless steel, nickel based alloys etc. The reason for this change is the rise in temperature which occurs at high speeds due to kinetic heating, and this rise in temperature is the condition which influences the choice of materials, paint included.

When a body moves through the atmosphere the air is deflected around it except at a point immediately in front of the body, known as the "stagnation point" where the air is brought to rest. Owing to compressive effects, the temperature of the air rises at this point. The temperature attained at this point is called the stagnation temperature.

A complex equation to give the stagnation temperature can be derived from a knowledge of specific heats of air at constant pressure and temperature and the Mach number. This can be reduced to a useful approximation:

$$(T_S - T_A) = \left(\frac{V}{100}\right)^2 {}^\circ C$$

T_S = Stagnation temperature
T_A = Free stream temperature
V = Velocity in miles per hour

The temperature of the structure will, over long soak periods, approximate to this temperature. A number of other factors will enter into the calculation of the actual temperature, including the amount of radiation received from the sun, the emissivity of the surface etc. By controlling reflectance and emissivity, the paint itself will make a contribution, albeit relatively small, to the final temperature of the structure. (see Fig. 1)

In a practical case, a Mach 2.2 aircraft flying at 60,000 feet is likely to develop a surface temperature of about 120°C. A paint with a reflectance over 75 per cent and an emissivity of 0.8 has been calculated to contribute a reduction of 10°C in the final soak temperature of the structure. This is not insignificant at a fairly critical point in the properties of traditional aircraft materials.

The fundamental problem in high speed aircraft is that of heat. Paints must withstand the effects of this in order to perform their necessary functions and may also be required to have characteristics to mitigate the effects of the heat. In the latter case, the characteristics which give the paint its special properties must remain substantially constant under its conditions of service—including continual heating.

It is probably convenient now to divide paints into categories according to the temperature at which they are required to operate. It should be borne in mind that it is really the time/temperature combination which is important and not temperature alone. Fighter and bomber aircraft may, indeed, be very fast, but their higher speeds may only be achieved for relatively short times when they are using their "dash" capacity. Transport aircraft, on the other hand, may spend many hours at relatively high temperatures. By and large, at the moment, it is the latter case which is the more difficult to meet.
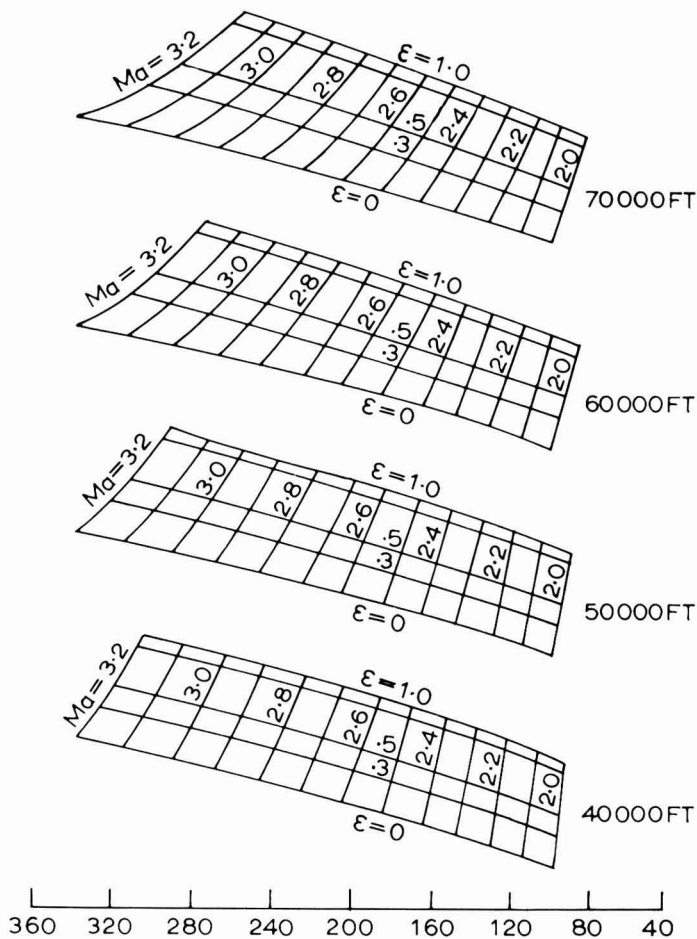
Fig. 1. Equilibrium temperature, (T_E) °C, for various values of emissivity (ε) (evaluated for point 10 ft. from leading edge). (Crown copyright, reproduced by permission of the controller of H.M. Stationery Office)

It should be stressed that there are many operational requirements which influence the choice of paint schemes and, as always in paint technology, the chosen material is likely to be a compromise.

On an aircraft one has always to consider the fluids used for various purposes. There are the fuels, hydraulic fluids, lubricants of various sorts. The fuels are almost invariably hydrocarbon, kerosene, petrol, etc., although isopropyl nitrate may briefly be encountered for starting. The fuel may well include small quantities of other ingredients such as ethylene glycol monomethyl ether, but basically they are hydrocarbons and, if rocketry is excluded, this will apply to subsonic and supersonic aircraft alike.

The hydraulic fluids can be hydrocarbons for instance mineral oil to DTD585, phosphate esters of the Skydrol type, ethylene glycol monomethyl ether castor oil mixtures, silicone oils or silicate esters. The temperature envelope of the

aircraft will influence the choice of hydraulic fluid very markedly. Mineral oils are most commonly used in the subsonic region on military aircraft and even some way into the supersonic range. Civil airlines will probably use phosphate ester or ethylene glycol monoethyl ether/castor oil fluids in the faster subsonic aircraft, although the reasons are probably more concerned with fire risks than the actual operating temperatures. In the supersonic region, chlorinated silicones or silicate esters are likely to be used. Since there are likely to be quantities of these substances around because of leakage, good resistance will be required—a paint floating on top of a pool of hydraulic fluid will not be much use in protection against corrosion.

Engine lubricants, too, will vary according to aircraft type, but they are more related to engine temperatures, which tend to be hotter the more efficient the engine, rather than to the kinetic heating which influences the rest of the aircraft. It is an unrelated fact that the faster aircraft require more powerful engines which tend to be hotter. The division into types here is mainly between piston engines, which use hydrocarbons, and gas turbines, which use ester lubricants. The concern here is not with piston engined aircraft, which are never supersonic. The ester lubricants are mainly di-esters of various types. Di-butyl phthalate or sebacate typify the class, but it should be borne in mind that various mixtures are used and other materials such as various anti-oxidants are present as well. It is not only the original di-ester which may be a hazard to paint work, but also the various breakdown products which occur on heating in the engine. Pyrolised oils contain complex mixtures of octenes, ketones, acids etc which are very aggressive to paint.

Finally, one should not forget that diabolically destructive aircraft fluid— water. During the flight cycle, humid air taken in on the ground is rapidly cooled and condensation takes place which collects in various places. In a supersonic aircraft, as the speed rises the temperature will rise also and the temperature of the liquid water with it until boiling may occur. For a short time boiling water conditions may be encountered. This pattern will be repeated on every flight. Thus intermittent exposure to boiling water is a hazard that the internal paints may have to face in certain areas.

There are not too many acute problems with aircraft which are not likely to become hotter than 100°C. Discoloration would occur with nitrocellulose and alkyd schemes, as would fairly rapid mechanical deterioration. They are not likely to be used for other reasons also. Epoxies will remain mechanically sound and their protective capacity will be unaffected, although the temperature will probably accentuate their discoloration a little. This is probably not likely to be very significant except for white topping and possibly some light greys. Aliphatic polyurethanes would be scarcely affected in any way and acrylics not at all. Neither polyvinyl butyral nor phenolic modified etch primers would have their properties seriously modified. In short, the types of schemes commonly employed for various reasons could be used both internally and externally. These would probably be epoxy primer pigmented with strontium chromate both internally and externally, possibly an epoxy finishing coat where appropriate on the interior, and either a polyurethane or acrylic finish on the outside.

The next temperature group, 100-130°C, is much more vital. This embraces the Mach 2.0 to 2.2 aircraft, and it is within this bracket that the Concorde falls. It is a particularly significant region because it is also the upper limit at which conventional aircraft construction techniques can be used. Aluminium alloys cannot, in general, be used as load bearing structures much above 130°C, at any rate if a fair margin of safety is to be allowed. It was mainly for these reasons that the choice of this speed range was made for the first generation supersonic aircraft. Accordingly, it is a range which has been intensively studied.

There are various aspects to the problem, and these will be discussed separately.

Interior paints

Obviously parts of the interior will be insulated and air conditioned, and requirements in these areas will be no different from subsonic aircraft. The other interior surfaces are in the uninsulated areas, the insides of outer skins etc. To a large extent such areas will be relatively inaccessible after the aircraft has been built. By and large, it should not be necessary to repaint after less than 40,000 hours, or something like ten years. A fair proportion of this time is likely to be spent at temperatures approaching 120°C. The ideal, therefore, is 40,000 hours at 120°C. The type of primer principally used on present aircraft is an epoxy/polyamide pigmented with strontium chromate. It is designed to leach out traces of chromate slowly to provide inhibition for the protection of the metal over long periods. It has performed well, and is highly resistant to most aircraft fluids. The first question is whether this type of material is suitable at 120°C. Apart from discoloration, the epoxy/polyamide remains mechanically sound and highly protective for prolonged periods at this temperature; so far as the medium is concerned there is no problem. Difficulties arise in connection with the pigmentation when the boiling water condition is encountered, however. Chromate may be leached out too rapidly and the film weakened mechanically and depleted too soon of available chromate. It has been considered desirable to switch from the slightly soluble strontium to the relatively insoluble barium chromate and rely on the higher leaching rate of the latter under conditions prevailing at higher temperatures.

It would be helpful to designers if the emissivity of interior coatings could be reduced. Practically all organic coatings have relatively high emissivities, certainly above 0.8, largely due to the absorption bands in the far infra-red which are present in all polar organic compounds. It does not appear to matter a great deal if the pigmentation is matt or not. Certainly, at practical levels of pigmentation there is sufficient medium present to keep the radiation high (quite apart from any effects from the pigment). Emissivity can, however, be reduced by using laminar pigments such as aluminium. Providing this leafs well, the emissivity can be reduced to 0.4. Difficulties arise, however, as the aluminium ages, and the emissivity rises to about 0.7. Designers need, of course, to allow for the worst conditions, so that no weight saving is possible here. Certain copper bronzes can be used to give the same effect and are relatively stable. The dangers of using bronzes in close proximity to aluminium are only too apparent and the fear of electrochemical corrosion in inaccessible

areas rules out their use. In any case, the surface need only become lightly contaminated with oil or dirt and the emissivity rises to the level of the contaminant. Since it would be impossible to maintain the surface clean in practice, this is not considered a likely technique, but it is of interest and has been considered.

Interior finishing coats will be epoxy/polyamides but in most of the areas primer-only schemes are likely to be used, although multiple coats of these may be employed.

Exterior paints

Exterior coats present a greater problem, because here there is value in high reflectance and high emittance, and the aesthetic requirements demand negligible discoloration. The apparent paradox of requiring high reflectance and high emittance is explained by the facts that reflectance is from a source of radiation at 6000°K (the sun) and emission from a surface at a temperature of 390°K (the temperature of the structure). Epoxy/polyamide primers pigmented with strontium chromate are used, since there is no likelihood of boiling water, and the primers can thus be the same as on conventional aircraft.

Problems arise in connection with the finishing schemes. For prolonged periods at 120°C, the best materials are the acrylics, and next the aliphatic polyurethanes. Both however have defects. Acrylics are thermoplastic and tend to be indifferent in their resistance to aircraft fluids. To minimise defects in these respects, formulations tend to be based on methyl methacrylate and highly polymerised. Plasticisers (like butyl benzyl phthalate) may be used but, for obvious reasons, are kept to a minimum. The result is a low solids paint with a tendency towards brittleness which, even so, is minimal in fluid resistance. If soft comonomers are used to plasticise the methyl methacrylate (like butyl or ethyl hexyl methacrylate) then fluid resistance tends to be adversely affected. If the molecular weight is reduced, the polymer tends to be more thermoplastic. The basic thermal and light stability of the acrylics is due to their essentially polyethylenic backbone. Increasing molecular size reduces the solubility and hence increases fluid resistance. Hence, copolymers incorporating butyl or other monomers would have to have a very high molecular weight. Moreover, high molecular weights tend to increase feathering and other spraying defects. Attempts have been made to overcome these defects by copolymerising methyl and butyl methacrylates and by using pendant groups which could later co-react to give a highly cross-linked structure. Many systems have been tried, and it has been found that several pendant groupings de-stabilised the polyethylene chain and hence affected the heat and light stability. A carboxy/epoxy combination was found to be free from this defect and interesting systems on these lines have been prepared and tested. Unfortunately, compatability difficulties have given rise to storage problems, and the short shelf-life does not allow them to be a practical proposition at the moment.

Polyurethanes formulated from hexamethylene di-isocyanate adducts have a fair measure of stability to heat and are extremely lightfast. They have excellent resistance to aircraft operating fluids, far superior to any other resin, and possess many advantages in respect of cleanability etc. At 120°C, however, they discolour rather too rapidly to be used for high reflectance whites.

A comparison of the reflectivities of various systems is shown in Table 1.

Table 1

Reflectances of various systems on exposure to a temperature of 120°C

Time at 120°C	% reflectance		
	Acrylic	Cross-linked acrylic	Polyurethane
0 hrs	93	93	92
100	91	90	86
1,000	88	88	76
10,000	70	70	

The position changes as the temperature falls, and at 110°C and below the polyurethanes become a usable proposition. In camouflage colours, the polyurethane could probably be used at 120°C, but it would be very much a borderline case.

The discoloration of the polyurethane is accompanied by oxidative changes, and it is possible to inhibit this by the use of high temperature anti-oxidants. Unfortunately, these compounds, which are N, N¹ substituted phenylene diamines, e.g. N, N¹-di-sec butyl-*p*-phenylene diamine tend to discolour on exposure to light, so that the gain in one direction is counterbalanced by a loss in another. An interesting observation which has recently been made is that the coloured bodies produced by heat are discharged fairly quickly by exposure to sunlight, and it is open to argument as to which will be the dominant characteristic on a long flight in sunlight. Certainly for military aircraft, which spend less time at high speeds, the bleaching characteristics will be dominant. Long range transport aircraft are a different matter.

Although supersonic transport aircraft are currently painted with the polymethyl methacrylate type of finish, it is known that the indifferent resistance to aircraft fluids and the thermoplasticity of this coating are likely to give rise to staining in certain areas where spent hot engine oils impinge and where the fluid resistance and easy cleaning of the polyurethane would be invaluable.

It should be mentioned that it is axiomatic that any system for the exterior of an aircraft must be room temperature curing. Although a certain amount of stoving is carried out at the detail stage, final painting is invariably in a hangar which can, at best, only be kept warm. This is regrettable, because without doubt the thermosetting acrylics would solve a number of problems if stoving were practicable.

Jointing compounds

The main painting scheme has so far been considered. There are other compounds of a paint-like nature used on aircraft in much smaller quantities but vital to the corrosion protection.

Although basically made of aluminium, aircraft are, in fact, complex assemblies of dissimilar metals. It is vital to assemble the structure wet with

suitable jointing compounds. In a pressurised structure, many of the joints will of necessity be filled with pressure sealants. It is not proposed to deal with these, nor the sealants for the integral fuel tanks, although where they are used they will do the double duty of protecting against corrosion as well. There will be other areas where neither pressure nor fuel will be involved. In these cases, the ideal jointing compound is one which is of a suitable consistency for application by knife or brush, which does not shrink, is inhibitive, will conform to changes in the joint dimension without cracking, will not weep out of the joint under the influence of heat and vibration, and whose consistency will remain unchanged throughout its life so that when the structure has to be broken down for inspection or repair no difficulty is experienced in dismantling and no resultant damage to the structure occurs. Probably jointing compounds for "cool" aircraft do not achieve the ideal, but in practice they approximate to it. A number of problems arise when heated structures are considered. In the first place, the current polyester types oxidise, harden, and crack at 120°C. In the second place, it becomes difficult to reconcile the retention of a permanently plastic nature with freedom from weeping out of a joint under heat and vibration, particularly when the application requirements are borne in mind. Most resins which do not oxidise, cure or harden in any way on heating fall considerably in viscosity between room temperature and 120°C and their vibration and mechanical stability suffer accordingly. If the consistency is chosen so that it is satisfactory at high temperatures, then it will be very viscous at room temperature and considerable quantities of solvents will be required to enable satisfactory application. This may lead to shrinkage problems. The formulation of a satisfactory compound involves finely balancing the various conflicting requirements. Attempts have been made to formulate such materials using non-curing fluorocarbon resins and controlling the rheological characteristics by means of fibrous pigments. The problem has proved somewhat intractable, and aircraft have been designed to minimise the areas which must be broken down at intervals to those where fairly stout bolts are involved.

Erosion resistance

The problem of erosion resistance should also be considered. When an aircraft flies through rain at high speeds, considerable erosion of all strike surfaces takes place and protection of these may be necessary. In extreme cases, it may be necessary to design the aircraft with stainless steel strike surfaces, and these will be unpainted. It is quite impossible to keep paints on under the worst conditions. The behaviour of a raindrop on impact largely depends on the velocity of impact. With impact velocities up to 1,000ft/sec, a water drop behaves like a hard projectile on impact, but retains its liquid property of flow. At greater velocities, the drop behaves progressively more like a hard projectile which does not flow as a result of the collision. Tests have shown that a drop colliding with aluminium at 2,000ft/sec makes an impression like that made by a low velocity steel sphere. When collision occurs between a raindrop and the surface of a solid, the impact pressure rises rapidly to a high value, driving the liquid that is close to the solid surface radially outwards round a central stagnation point. The moving liquid is in laminar flow and the resulting pressure increases with the size of the water drop. It has been estimated that an impact pressure of 30,000 psi can occur at an impact velocity of 600 mph (880ft/sec) and the radial flow of liquid attains a

velocity of about 1,400 mph (2,053ft/sec). The radial flow of the raindrop exerts a shear stress on the surface over which it runs, and between the separate layers of water in laminar flow. If a small protrusion exists in the surface, these forces tend to move it along the surface and this produces a shear stress in the surface; if this is greater than the tensile strength/adhesive strength of the material, tearing and stripping will result.

The forces involved are, at velocities above 500 mph, greater than can be withstood by normal paint coatings, and erosion takes place. Indeed, from about this point erosion of the aluminium starts to become significant.

If an elastomeric coating of sufficient thickness is applied, however, then the shock can partially be absorbed by the coating. Neoprene coatings have been used, but they suffer from the difficulty of repairing damage when it does occur. Elastomeric polyurethanes are rather better in this respect and also for erosion resistance, but as they have to be applied from solution to give a total film thickness of over 0.020in, and as an hour must elapse between each coating (each less than 0.001in) it is an exceedingly tedious business to apply them in this field. Incidentally, supersonic aircraft are not likely to fly through heavy rain at very high speeds since these are normally only achieved at high altitudes. They are, however, likely to encounter rain at speeds of 500-600 mph, which is pretty fast by any standards.

Future developments

Some speculation on the future is of interest. Fig. 2 shows the relationship between temperature and Mach number, and it will be seen that a small increase in Mach number from 2.2 to 2.5 raises the stagnation temperature by over 70°C to around 200°C. At Mach 3.0, the temperature is 330°C and in fact the relationship given earlier ceases to be valid at this point. The metals used will, of course, be different. At 150°C, the acrylics used at present will be markedly softened, although there is every chance that they will withstand such a condition at least for a time and, in fact, peaks of this order may well be encountered now. At higher temperatures, they will cease to be useful. It would be possible to use silicones up to about 250°C, although as a class they have poor resistance to hydrocarbons. There might well be curing problems. Incidentally, the argument that one could apply paint and then fly the aircraft will not hold. There is a long gap before flight, and the fluids and manhandling are there continuously long before a useful curing temperature is achieved.

At the higher temperatures, organophosphates or silicates might be useful. Both have been studied but both suffer from many defects. They are brittle, and adhesion is poor. If stoving could be considered, polyimides or polybenzimidazoles might be possibilities, and cold curing techniques have been tried but, although nominally curing, the high temperature stability appears to be adversely affected.
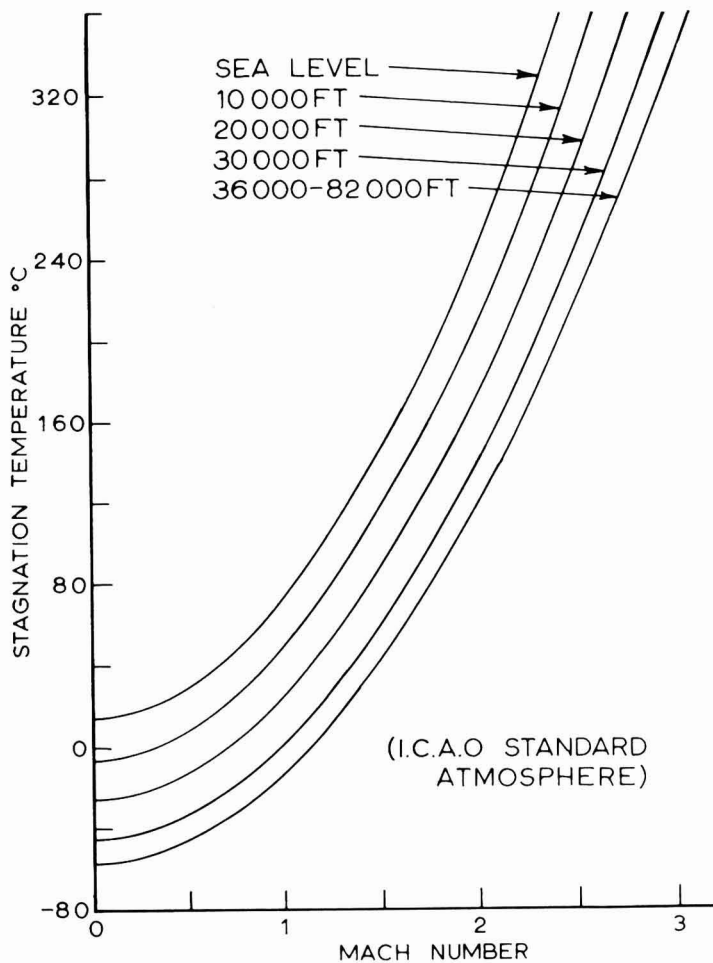
Fig. 2. Variation of stagnation temperature with Mach number. (Crown copyright, reproduced by permission of the Controller of H.M. Stationery Office)

At Mach numbers only a little higher than 3.0, the surface becomes red hot and speculation on the nature of coatings becomes inextricably associated with speculation on the nature of the substrate and possibly even on the nature of the aircraft itself. The future is not without its problems.

Evaluation of the effect of the steel base and polyethylene coating properties on the bond strength of the system polyethylene coating/ steel base

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Summary

The widest area of application for polyethylene coatings is the protection of metal surfaces against corrosion. Preparation of high-quality coatings and determination of their range of application require a thorough knowledge of the factors determining the properties of the system, polyethylene coating/metal base. In the first place, it is necessary to be aware of initial properties of the system and the changes occurring under non-corrosive conditions. This work deals with the evaluation of the effect of the steel base properties and properties of the physicochemical structure of the polyethylene coating on one of the fundamental properties of the system, i.e. on the adhesive-cohesive strength of the bond between the polyethylene coating and a steel base.

Keywords

Types and classes of surface	*Binders—resins etc*
steel	polyethylene

Properties, characteristics and conditions primarily associated with dried or cured coatings	*Process and methods primarily associated with analysis, measurement and testing*
adhesion	peel test

L'évaluation de l'effet du support en acier et des propriétés du polyéthylène sur la force de la liason entre le support et le revêtement à base du polyéthylène

Résumé

Le domaine le plus étendu pour l'application des revêtements à base du polyéthylène s'agit de la protection des surfaces métalliques contre la corrosion. La préparation des revêtements de haute qualité exige-t-elle une connaissance complète des facteurs qui déterminent les caractéristiques du système revêtement polyéthylènique-support métallique. Auparavant il est nécessaire de connaître les caractéristiques initiaux et les changements qui arrivent sous des conditions non corrosives. Cette étude se traite de l'évaluation de l'effet qu'exercent les caractéristiques du support métallique et à la fois la nature de la structure physico-chimique du revêtement polyéthylènique sur une des propriétés fondamentales du système, c'est-à-dire, sur la force adhésive-cohésive de la liason entre le revêtement polyéthylènique et le support en acier.

Bewertung des Einflusses der Eigenschaften von Stahlsubstrat und Polyäthylenüberzug Hinsichtlich der Bindungsstärke des Systems Polyäthylenschicht-Stahlsubstrat

Zusammenfassung

Polyäthylenbeschichtungen werden am häufigsten zum Schutze von Metalloberflächen gegen Korrosion verwandt. Die Anfertigung von Beschichtungen hoher Qualität, sowie die Beurteilung des Bereiches ihrer Anwendbarkeit erfordern gründliche Kenntnisse der Faktoren, welche die Eigenschaften des Systems Polyäthylenüberzug-Metallsubstrat bestimmen. In erster Linie muss man die zu Anfang vorhandenen Eigenschaften des Systems, sowie die unter nichtkorrosiven Bedingungen vorkommenden Veränderungen kennen. Diese Arbeit behandelt die Bewertung der Auswirkung der Eigenschaften einerseits des Stahlsubstrates, andererseits der physikalisch-chemischen Struktur der Polyäthylenschicht auf die fundamentalen Eigenschaften des Systems, d.h. auf die adhäsive—kohäsive Bindekraft zwischen dem Polyäthylenfilm und einem Stahlsubstrat.

Оценка влияния свойств стали и полиэтиленовых покрытий на силу связи системы полиэтилен-металл

Резюме

Наиболее широкая сфера применения полиэтиленовых покрытий проявляется в защите металлических поверхностей от коррозии. Изготовление покрытий высокого качества и определение диапазона их применения требует доскональных знаний факторов опред-еляющих свойства системы полиэтиленовое покрытие–металлическая основа. В первую очередь необходимо учесть исходные свойства системы и изменения происходящие в нержавеющих условиях.

Статья оценивает влияние свойств стальной основы и свойств физико-химической структуры полиэтиленового покрытия на одно из фундаментальных свойств системы, а именно на адгезионно-сцепляющую силу связи между полиэтиленовым покрытием и стальной основой.

Part 1. Theoretical fundamentals, materials and methods of evaluation

The method of peeling off the coating by the use of force, acting in the normal direction to the base surface, is among the methods most frequently used for the evaluation of the adhesive properties of coatings. The work necessary to separate the coating from the steel base may be theoretically calculated from the force measured.

$$W_a = P(1 - \cos \theta)$$

W_a specific adhesive work

P force necessary to peel off the coating

θ angle at which the separation takes place

In the case where $\theta = 90°$, then $W = P$. Nevertheless, this correlation may be fulfilled practically only under conditions of equilibrium. However, the failure of the bond existing between the coating and the steel base never occurs under conditions of equilibrium. In certain instances, when perfectly elastic coatings have been used and a very low speed of peeling off the coating employed, it is possible to approach conditions conforming to the validity of the above correlation. Measured results then approximately agree with the equation.

The modified relation that includes the deformation work of the film, verified for the system polyvinyl acetate/polyisobutylene/glass, has been mentioned by Hata[1].

$$W = P \left(\frac{(\lambda + 1}{2} + \cos \theta \right) = P \left(1 - \cos \theta \right) + \frac{P^2}{2t_o E}$$

P = measured force
W_a = specific adhesive work
λ = percentage elongation
t_o = film thickness
E = Young's modulus of elasticity

The above relation is, however, not applicable to the normal case, as it does not include, for example, the effect of the stress inside the coating and the undefinable stress concentration occurring, especially at the point of the separation. During the formation of the coating, relatively high interfacial surface tensions develop in the interface between the polymeric coating and the steel base which are in direct relation to internal stresses occurring in the coating. Internal stresses in the coating are mainly caused by differences in the thermal expansions of the polymer and steel.

For these internal stresses, the following relation may be derived within the limits of the validity of Hooke's law.

$$\sigma_p = \frac{E_p (\alpha_p - \alpha_k) (t_1 - t_2)}{1 - \mu_p}$$

E_p — modulus of elasticity of the polymer
α_p coefficient of thermal expansion of the polymer—so long as no changes of the crystallinity occur simultaneously with the change of the polyethylene temperature, this coefficient equals 2.5×10^{-4} °C^{-1}, while in the region of the crystallinity degree changes, its value approximately doubles
α_k coefficient of the thermal expansion of the metal (steel approximately 1.4×10^{-5} °C^{-1})
$t_1 - t_2$ = temperature difference
σ_p = Poisson's ratio (0.4 for most plastics)

For the interfacial surface tension proper, Makuskin[2] has derived a complicated relation which takes into consideration the shape and height of unevennesses in the metal surface as well as the surface hardness. These tensions in the system coating/steel act against the cohesive and adhesive forces. They reduce the force measured during the separation of the coating from the base.

Some of the earlier workers (Huntsberger[3], Brunt[4]) have tried to eliminate the unfavourable secondary effects of the real system in order to obtain data which would be closer to the adhesive forces required. They did so by comparing the quantitative relationship existing between the deformation velocity, temperature, specimen geometry, composition of the coating, etc., on the one hand, and the measured peeling force, on the other hand.

From the above survey, it follows that, when using any of the means of causing failure considered above, the adhesive properties alone cannot be determined except the whole complex of properties of the system. Therefore, it is not considered reasonable to discuss adhesion as defined by specific quantities, except in terms of the bond strength of the system coating/steel base, together with the characteristics of the method of force application. Such values may not only be used for the analyses of certain systems, but they are also of great importance in practice.

The present work is aimed at the investigation of the effects of the properties of the steel base and the polyethylene coating themselves on the bond strength of the system, when the polyethylene coating is applied by melting the pulverised polyethylene on the heated steel base. In this case, it was possible to obtain correlation with some of the factors already described.

During the preparation of the polyethylene (PE) coating, the steel surface is always covered with oxides of iron, and contaminated with particles from the surrounding atmosphere. Bright[5] states that polyethylene adheres to the metal through a highly condensed thin layer of molecules of water on the surface. On the basis of this assumption, he explains the reversibility of the initial bond strength after exposing the system PE coating/steel to humidity and redrying. Notwithstanding the facts above mentioned, the first prerequisite of a good adhesion is probably to obtain best physical contact of the coating with the steel base. Kalnin[6] studied the problem of attaining the most perfect contact between the PE coating and metal base, and found that the conditions needed were less exacting than those demanded for the necessary oxidation of polyethylene. However, it is certain that the final physical contact will be dependent on the roughness of the surface, and also dependent on the type of polyethylene used, as well as on conditions existing during the solidification of the coating.

The authors of a number of papers on this subject agree that oxidation of polyethylene represents the most important factor in obtaining good adhesive properties[5,7,8,9,10]. Bright[5] shows the importance of the catalytic effect of the base metal on polyethylene oxidation. The proof of oxidation of polyethylene is demonstrated both by referring to the change of the surface energy of polyethylene[9] and by infra-red spectroscopy[10]. During experiments in which it was shown that oxidation played an important part in the adhesion to the steel base, it was observed that failure occurred in the surface layer of polyethylene and traces of it remained attached to the metal surface. Bickerman[11] explains this fact by the presence of low-molecular fractions in the polyethylene, and proves that by extracting these fractions, the bond strength increases. Nevertheless, Bright[5] proves that the oxidation of polyethylene is of substantially greater importance than the extraction of of low-molecular fractions. There is, however, no generally accepted explanation for the cohesive failure of the bond. A more common explanation, suggested also by Bickerman, might lie in the fact that the low strength of the surface layer of polyethylene is caused by the high internal stresses which form therein.

From a survey of the present knowledge on the subject, it is evident that the bond strength of the system PE coating/steel base must be significantly influenced by the quality of the steel-base material, as well as by the physicochemical

properties of the PE coating. The problem of to what extent individual effects are of importance will be evaluated in this work.

Materials used

Low-density polyethylene "Telcothene," manufactured by Telcon Plastics, was used for the preparation of coatings. The density was $0.92 g.cm^{-3}$, the melt-flow index (ISO R 317-61) $18 g.min^{-1}$ and the melting point range 112-115°C. The base used in the experiments was cold-rolled steel sheet to CSN (Czechoslovak State Standard) 11320.

Preparation of specimens

The specimens used in the strength measurement were prepared from 20mm wide and 1mm thick steel strips bent into a semi-circular shape having a diameter of 90mm. The specimens were first degreased in trichlorethylene and then grit blasted under standard conditions with sharp steel grit of a given grain size. As soon as the blasting had been completed, the specimens were stored for at least 24 hours in a desiccator above a desiccant (molecular sieve NALST 4). Prior to the application of polyethylene, the metallic specimen was resistance heated and oxidised with atmospheric oxygen to a chosen degree and then maintained at a selected temperature; polyethylene was then applied to it using a fluidisation method. The applied polyethylene powder was finally fused for a given time.

The standard treatment was as follows: blasting was carried out with sharp steel grit No. 90 (screened to the grain size 0.1 to 0.2mm) under a pressure of 2.5atm from a distance of 30cm; oxidation of the steel specimen to oxide was judged by a gold interference colour (attained after an approximately 75 seconds heating from room temperature up to the maximum temperature of 290°C); temperature of the steel specimen during the melting of polyethylene was 245°C, melting-through time 5 minutes. The thickness of PE coating was $1.1 \pm 0.15mm$. Fluidisation and melting were carried out either in air or in an atmosphere of nitrogen of the quality used for incandescent lamps (below 0.1 per cent O_2). After preparation, the majority of specimens were subjected to a further thermal or thermo-oxidative treatment. Heat treatments were carried out either in air or an atmosphere of nitrogen at temperatures above the melting region of polyethylene, i.e. at 120°, 135° or 150°C. The average heating time of specimens at a given temperature was 45 minutes. Various cooling rates were obtained by:

immersing the specimens in a mixture of butanol and solid carbon dioxide, at −60°C   (A)

immersing the specimens in a mixture of butanol and solid carbon dioxide, at +15°C   (B)

cooling in a drier at a cooling rate of approximately $1°C.min^{-1}$ (C)

free cooling in air at a cooling rate of approximately $7°C.min^{-1}$ (D)

After preparation, the specimens were stored in a desiccator over a molecular sieve.

Films for the control measurement of the mechanical properties of polyethylene were prepared by the same method as used for the preparation

of specimens designed for bond-strength measurements for the system PE coating/steel base, but on a Teflon-coated base. From the films, special dumbbell type tensile test specimens were then stamped.

Specimens to be used for the infra-red spectroscopy were prepared by pressing from 18 × 15mm strips that had been cut from the specimens used for measuring the strength of the bond. The pressing was carried out in a miniature mould at 160°C in a nitrogen atmosphere for 25 minutes. Cooling of the films was carried out in closed moulds in air. A reference specimen was prepared in the similar way from tabletted polyethylene powder. The thickness of the films was 130 ± 20μm.

Evaluation methods
Measurement of the bond strength of the system PE coating/steel base, and evaluation of the adhesive properties of the coating: The strength of the bond between the PE coating and steel base was determined by the force necessary to peel off the coating.

In the central part of the specimen described earlier, an 8mm wide strip of the coating was separated by cutting through the film along the whole circumference of the specimen. The specimen was fixed on a circular fixture and the loosened strip of coating was gripped in the jaws of the tensile strength tester (ZT 10, VSB Thüringen Industrie Werk, Rhauenstein). The force necessary to peel off a strip of the coating, acting in the direction normal to the tangent plane of the circular specimen, was measured. From the test record, the mean value of the peeling force, was calculated. The measurement was carried out at the cross head speed rate of 50mm.min^{-1} and a temperature of 23 ± 2°C. Three specimens were measured simultaneously. The statistically determined variability of the measured and calculated values of the peeling force did not exceed 10 per cent.

The method of measuring the strength of the bond between the coating and metal by peeling the coating required a more particular analysis.

One cannot, however, judge unequivocally the adhesive properties of the coating by simply considering only the peeling force necessary. It has already been mentioned that visible traces of polyethylene remained sticking to the steel base after the separation. After the peeling off of the coating, the metallic base exhibited the appearance of chamois leather when viewed from a certain direction. From the photomicrograph of a cross-section made through the coating (see Fig. 1) it may be seen how the failure of the boundary layer takes place after deformation. After a reduction of the bond strength, e.g. by immersing the specimen in water, the uniform chamois leather-like appearance of the metal surface gradually becomes less apparent. The proportion of the polyethylene adhering to the surface progressively diminishes until finally only an entirely metallic surface remains. There is no unambiguous explanation of the causes of the cohesive failure of the PE coating interfacial layer. In this work, the author has not studied the problem in detail. One thing is, however, sure, that the measured values of the strength of the bond between the PE coating and the steel base are proportional to the adhesive forces between the coating and base on the one hand, and the cohesive properties of the PE coating, especially of its boundary layer, on the other hand. It can thus be stated that

Fig. 1
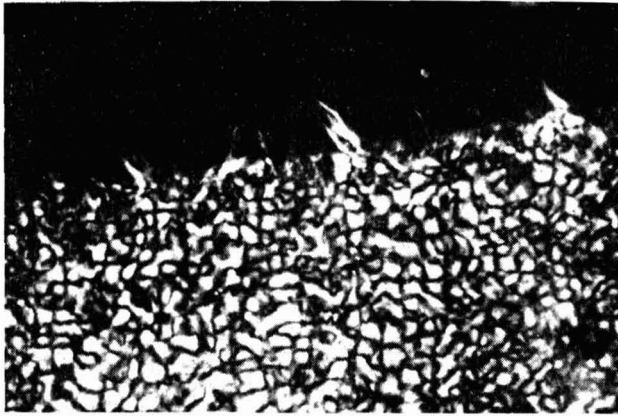
Fig. 2

Fig. 1. Photomicrograph of the cross section of the polyethylene coating. Failure of interfacial layer, occuring at the separation of the coating from the base; microscopic magnification 200 ×, photographic magnification 4 ×

Fig. 2. Geometry of the peeling of polyethylene coating. Peeling force 1.2 kp

the adhesive-cohesive properties of the system are a combination of these factors.

In the case of the polyethylene coating evaluated in this work, it is not possible to convert the measured peeling force values to a specific strength quantity which, for example, in this case is definable in units of work. At the point of failure of the bond, the coating being separated does not make a precisely definable angle with the tangent plane. When the same manner of loosening the PE coating is employed, then, depending on the adhesive or adhesive-cohesive forces, on the internal stresses acting against these forces and on the visco-elastic properties of the coating, the loosening of the coating takes place at various angles and is accompanied by various displacements of the force from the area of separation. The stress concentration in the separation area changes. When carrying out certain relative investigations, it is not necessary to consider the effect of these factors. From Figs. 2, 3 and 4 it may be seen how,

Fig. 3
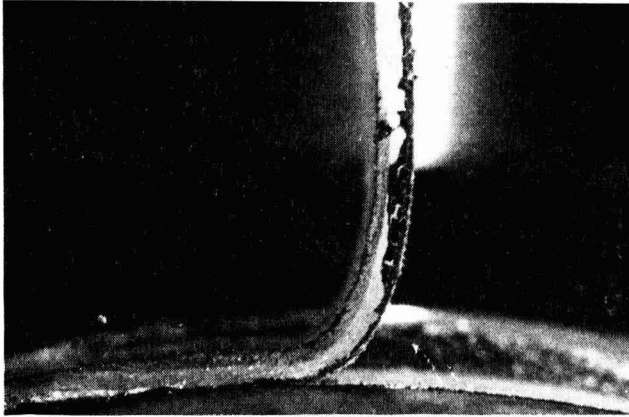
Fig. 4
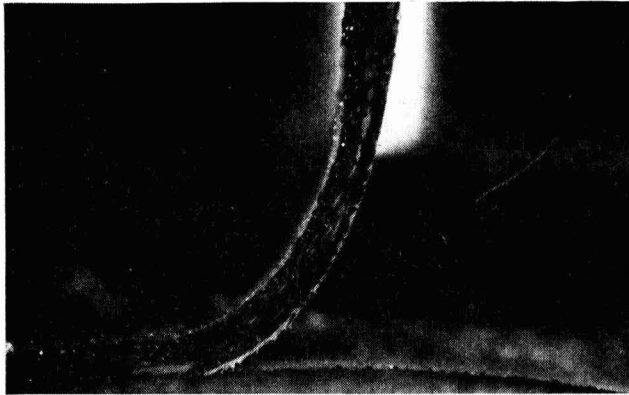
Fig. 3. Geometry of the peeling of polyethylene coating. Peeling force 0.8 kp

Fig. 4. Geometry of the peeling of polyethylene coating. Peeling force 0.2 kp

as the bond strength decreases by the penetration of water into the coating/
metal interface, P_o, the measured peeling force, decreases in parallel with the
decrease of the separation angle and increase of the moment of acting force.
Taking into consideration the minute weight of water absorbed by the
PE coating, it may be assumed that the viscoelastic properties, as well as the
internal stress existing in the coating, does not change, so that the measured
change is caused by the change of the ratio between the bond strength of the
system PE coating/steel, and the stiffness in bending of the coating of a given
thickness. The measured peeling force may be taken as the rate of the decrease
of the adhesive-cohesive strength of the bond. For purposes of comparison, the
effect of the PE coating thickness on the measured peeling force was determined.
At identical adhesive-cohesive properties of the coating, the stiffness in bending
of the coating changes. The relationship is represented in Fig. 5. The peeling
force increase follows approximately linearly the increasing bending moment
of the coating. The "line" slope is small.
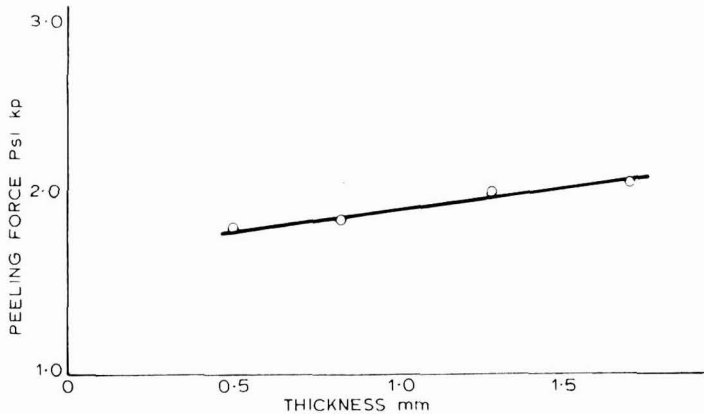
Fig. 5. Dependence of peeling force on the thickness of the polyethylene coating

From the facts mentioned above, it follows that, in coatings of given dimensions exhibiting constant viscoelastic properties, the relative adhesive-cohesive bond strength may be evaluated with respect to the peeling force. In the case where the viscoelastic properties of the coating change with the stress in the system, the measured peeling force is not necessarily proportional to the adhesive-cohesive properties, and the measured results are valid only for a similar strain application up to the point of failure.

Measurements of the coating properties
Measurement of mechanical properties: The mechanical properties of the PE coating were measured on tensile test specimens. The tensile test specimens were stamped by means of a die from the foils prepared in the manner already described. The width of the working part of the die was 5mm, length 20mm, the ratio of head to working part was 3:1. The measurement was carried out at the same speed and temperature as the measurements of the bond strength of the system. The apparent modulus of elasticity was read off from the linear part of the record of the tensile test. The values quoted represent the mean of three determinations.

Measurement of the specific gravity and calculation of the crystalline fraction percentage: The specific gravity of PE specimens was measured by the "density" gradient in ethanol/water, calibrated with a set of glass floats at a temperature of $25 \pm 0.1°C$. Accuracy of the determination was $\pm 0.0003 g.cm^{-3}$. The specimens were sheared from the strips peeled off during the strength measurement of the bond in the system coating/steel. Three specimens, each of them taken from a separate strip, were used for each determination.

The crystalline fraction was calculated from the relation

$$\% X = d_c/d \times [(d-d_a)/(d_c-d_a)] \times 100$$

where

d = determined specific gravity of the specimen

d_c = specific gravity of the entirely crystalline polymer

d_a = specific gravity of the entirely amorphous polymer

From the published data[12], d_c for the same polyethylene $= 0.85 g.cm^{-3}$.

Microscopic measurements: For the observation of the spherulitic structure of the specimen, a polarising microscope "Meopta" was used. The magnification was 200×. The cross-section through the coating had a thickness of 30 to 50μm.

Infra-red spectroscopy: The spectrometric measurements were carried out on a spectrograph NKG-14 within the wave-number range 1000-2000cm^{-1}. The thickness of pressed films was 100-150μm. Each specimen was examined on the spectrograph in two different places:

in the central part of the film—in the area limited by the original dimension of the specimen prior to the pressing of the film—the original surface of the specimen was examined—"P";

along the film edges—material which had been squeezed out during pressing—the inside volume of the specimen was examined—"V."

Extinctions were evaluated in bands:

876 cm^{-1} for $>C = C<$ groups, 1,450cm^{-1} for $-CH_3$ and CH_2 groups and 1,720cm^{-1} for the $>C = O$ group. Comparable values, characterising the proportional content of individual groups, were obtained after conversion to a uniform thickness of 100μm.

Part II. Experimental results

The effect of the shape and size of the surface unevennesses, as well as the effect of the quality and thickness of the oxidised layer on the steel surface, is studied.

As stated in part I, for any given physico-mechanical properties of the coating, the measured peeling force depends directly on the adhesive-cohesive strength of the bond.

Table I shows the peeling-force values measured in systems where the steel surface is treated under standard conditions of blasting with sharp grit of varying sizes of grain. For the unscreened grit employed in the experiment, the direct relationship between the surface roughness, as characterised by the root mean square deviation, R_a, and the specific surface area is valid[13].

Table I

Effect of the steel surface roughness on the adhesive-cohesive strength of the bond in the system polyethylene coating/steel surface

Conditions of the coating preparation:
SH interference colour of the steel surface
melting temperature: 245°C
melting time: 5 minutes
heat-treatment: at 150°C for 40 minutes

Characteristics of the sample blasted with steel grit no.	R_a (μm)	Coating thickness (mm)	Peeling force (kp)	Variability (%)
90	1.4	0.97	1.35	8.3
90	1.4	0.96*	1.83	5.7
34	5	1.00	1.91	9.7
34	5	0.95*	2.39	2.2
16	8	0.99	1.70	9.1
16	8	1.00*	2.18	14.7

SH—light brown   *heat-treated sample

The results obtained for the non heat-treated and heat-treated specimens show that, for certain types of unevennesses, there is no direct relationship between the peeling force and the specific surface of the steel base. This phenomenon may be explained by imperfect filling of deep hollows by the polyethylene coating.

Table 2 summarises the effects of the thickness and quality of the layer on the steel surface. These results prove that the thickness over the range 100 to 1,200 Å and quality of the oxide layer do not have any effect on the adhesive-cohesive strength of the bond, if the specimens are prepared under standard laboratory conditions.

Table 2

Effect of the oxidic steel layer on the adhesive-cohesive bond strength of the system polyethylene coating/steel surface

Conditions of the coating preparation:

melting temperature: 245°C
melting time 3 minutes
heat treatment: at 150°C for 40 minutes
cooling rate "C"

Heating of the steel specimen max. temp./heating time	Interference colour	Coating thickness (mm)	Peeling force (kp)	Variability (%)
240 C/1 min	Š	0.86	1.44	11.0
270 C/1,5 min	SH	0.89	1.34	3.4
270 C/1,5 min*	SH	0.96	1.70	4.0
320 C/3 min	ČF	0.90	1.34	6·0
320 C/3 min*	ČF	0.98	1.53	4.5
350 C/3 min	ŠM	0.86	1.43	11.6
350 C/3 min*	ŠM	0.88	1.64	4.2
410 C/2 min	ŠII	0.91	1.38	3.4
420 C/2 min	M II	0.88	1.32	5.4

*heat treatment sample   Š—grey colour   SH—light brown   ČF—red-violet
ŠM—grey-blue   Š II—grey II interference order   M II—blue II interference order

The effect of an additional fusion and of the physical structure of the PE coating
The conditions of preparation are the decisive factors determining the degree of contact between the coating and base, as well as the physical structure of the coating. In cases where, owing to the conditions of the preparation of specimens, different viscoelastic properties of the coating exist, it is possible to determine solely the strength of the bond between the coating and metal in terms of peeling strength (see Part 1). In order to specify these effects, specimens of PE coating were prepared under standard conditions on steel bases which had also been previously treated by standard methods. To determine the effect of the degree of contact, the specimens were subjected to additional melting, referred to later as "heat-treatment," at temperatures maintained above the melting point of polyethylene, namely 120, 135, and 150°C, and these procedures were carried out for various lengths of time. To avoid oxidation as far as possible, the experiments were carried out in an atmosphere of nitrogen.

The initial physico-chemical properties of the system are determined by the

conditions of preparation. On storage, a change of initial properties takes place, depending upon the initial state and the storage conditions. The most striking changes are caused by further crystallisation of polyethylene in samples which have been cooled suddenly. Experiments with extreme rates of cooling were carried out in order to determine the necessary interval between the preparation of specimens and their measurement. The change in the peeling force with the storage time is shown in Fig. 6, whilst the extent of crystallisation during storage is indicated by the changes in the density, given in Table 3.
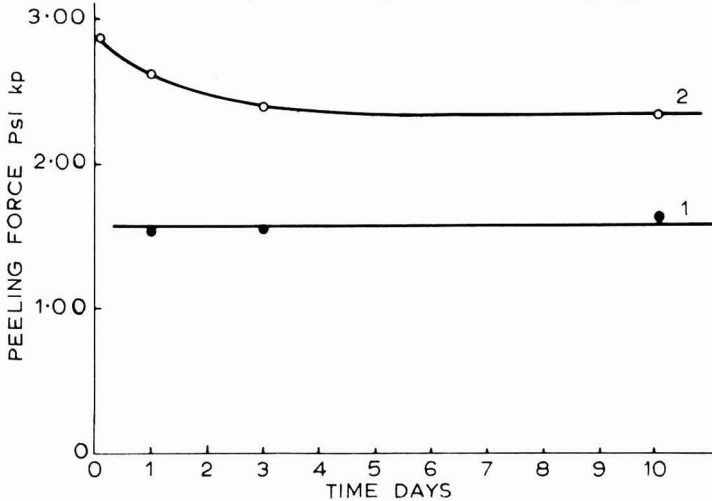
Fig. 6. Dependence of the peeling force necessary to separate polyethylene coating from steel base, on the storage time of the specimen in desiccator at 23 + 2 C

Melting temperature 245°C; melting time 5 min. in nitrogen atmosphere; heat-treatment temperature 150°C; heat-treatment time 45 min. in nitrogen atmosphere.
1—cooling rate "C."   2—cooling rate "A."

Table 3

Changes of the peeling strength of the polyethylene coating/steel base system in relation to the storage time in desiccator at 23 ± 2 C

Conditions of the coating preparation:
melting temperature: 245°C
melting time: 5 minutes
heat-treatment: at 150°C for 45 minutes in nitrogen atmosphere
cooling rate "C", "A"

Time from heat-treatment end (days)	"A" Peeling force (kp)	Variability (%)	Specific gravity	"C" Peeling force (kp)	Variability (%)	Specific gravity
0.08	2.86	7.7	—	—	—	—
1	2.60	8.9	0.9138	1.53	7.6	—
3	2.37	7.7	—	1.54	4.1	—
10	2.30	3.9	0.9149	1.59	7.7	0.9196

From these results, it follows that, after rapid cooling, the coatings show a considerably higher peeling strength, and even if the original strength decreases with further crystallisation during the storage, a significant difference remains for a long time. In accordance with these results, the interval between the preparation of specimens and their measurement was fixed at 7 days.

The results of a complex experiment to determine the effects of the additional heat-treatment and the physical structure of the coating on the peeling strength are summarised in Table 4 and shown graphically in Fig. 7. Table 4 includes also the corresponding specific gravities of the PE coating, and the percentage of the crystalline fraction as calculated from the specific gravity data.
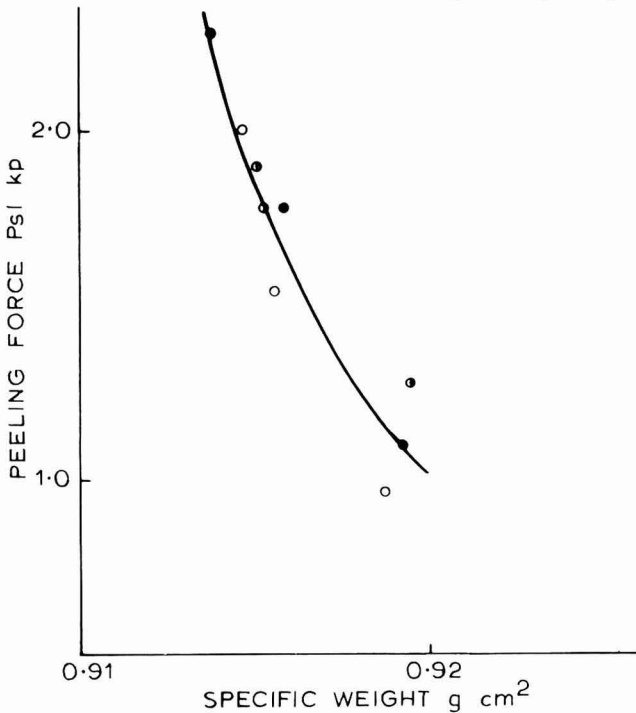
Fig. 7. Dependence of peeling force on the specific gravity of the polyethylene coating

Melting temperature 245 C; melting time 5 min. in nitrogen atmosphere; heat-treatment temperatures 120, 135, 150 C; heat-treatment time 45 min. in nitrogen atmosphere; cooling rates "A," "B," "C" (see Table 3).

When evaluating the effect of the heat-treatment process on the bond strength, it is apparent that the measured peeling force will involve the relative ratio of the adhesive cohesive strength of the bond. The effect of the additional heat-treatment time may be evaluated in quickly cooled specimens. The difference between the slowly and the quickly cooled specimens could be attributed to the different conditions existing during the formation of the coating. In the case of quick cooling, the coating exhibited a fine spherulitic structure, a lower degree of crystallisation, and a lower modulus of elasticity (see Table 5). Presumably, lower stresses arise during the solidification of the coating, which makes possible a more perfect contact between the coating and base. It may be

Table 4

Effect of the additional heat-treatment of coatings and their physical structure with relation to the cooling rate of the system on the peeling strength

Characteristic properties of the specimen after preparation			Heat-treatment conditions		Cooling method (rate) "A"			Cooling method (rate) "B"			Cooling method (rate) "C"		
Peeling force psi (kp)	Varia-bility (%)	Specific gravity	Temperature (°C)	Time (min.)	Peeling force (kp)	Varia-bility (%)	Specific gravity	Peeling force (kp)	Varia-bility (%)	Specific gravity	Peeling force (kp)	Varia-bility (%)	Specific gravity
1.12	12.5	—	120	45	2.28	3.6	0.9137	1.78	16.5	0.9158	1.1	6.5	0.9192
1.18	4 5	0.9189	135	20	1.66	8.5	0.9153	—	—	—	1.28	5.6	—
—	—	—	135	45	1.90	7.9	0.9150	1.72	2.3	0.9158	1.28	5.0	0.9194
0.91	9.4	0.9185	150	45	2.00	8.1	0.9146	1.54	8.5	0.9155	0.97	10.0	0.9193
Calculated mean values					2.08	—	0.9144	1.68	—	0.9157	1.11	—	0.9193

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assumed that an improvement of physical contact takes place in the melt during the additional heat-treatment; this improvement, however, is not certain to remain in the finished coating.

Table 5

Mechanical properties of polyethylene coatings when system PE coating/steel base is cooling by cooling rates "A" and "C"

Conditions of the coating preparation:

melting temperature: 245 C
melting time: 5 minutes in nitrogen atmosphere
heat-treatment: at 150 C for 45 minutes in nitrogen atmosphere

Cooling rate	Percentage elongation (%)	Stress at rupture (kp/cm²)	Yield stress (kp/cm²)	Apparent modulus of elasticity (kp/cm²)
"A"	300	85.5	69.3	1.0×10^3
"C"	95	82.0	94.0	1.7×10^3

As may be seen from Fig. 7, the effect of the heat-treatment temperature on the strength of the bond formed between the polyethylene coating and the steel base is not apparent. Figs. 12 and 13 indicate the spherulitic structure of polyethylene "heat-treated" at 120 and 150°C. It is more probable that after having been melted through at a temperature near the melting temperature, the coating structure becomes non-uniform, areas with a small number of crystalline nuclei alternating with others having a great number of such nuclei. As is shown by the dependence of bond strength on time, as in Figs. 8 and 9, greater changes of crystallinity take place in these specimens.
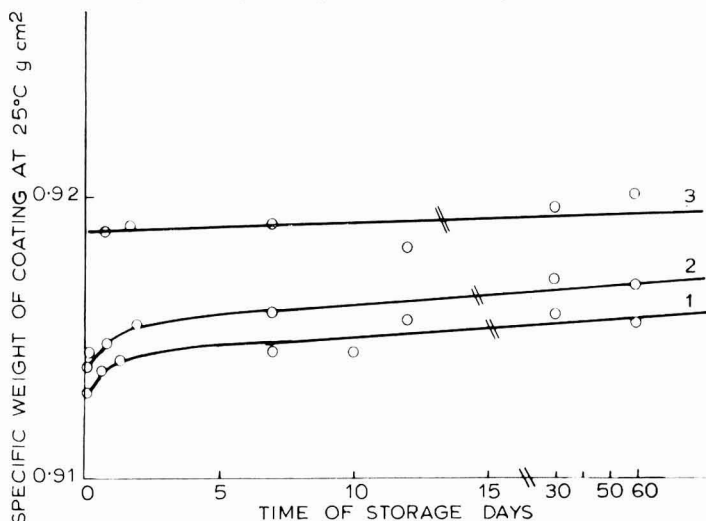
Fig. 8. **Change of specific gravity with time for polyethylene coating stored in desiccator at 23 ± 2°C**

Melting temperature 245 C; melting time 5 min. in nitrogen atmosphere; heat-treatment temperature 120 C; heat-treatment time 54 min. in nitrogen atmosphere.
1—cooling rate "A."   2—cooling rate "B."   3—cooling rate "C."
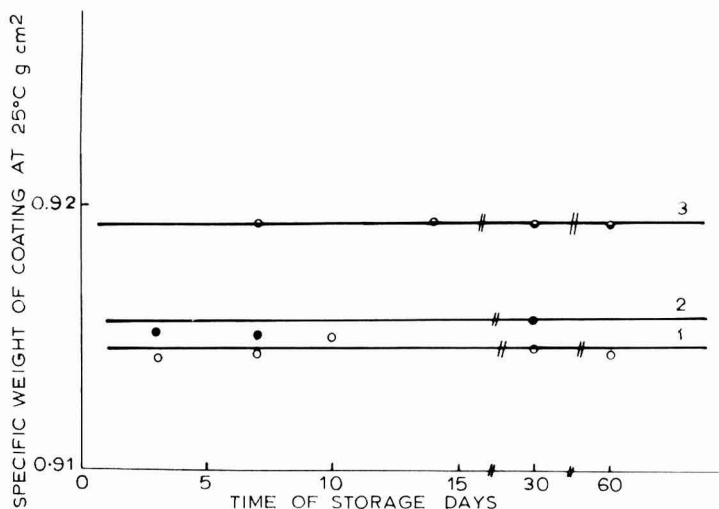
Fig. 9. Change of specific gravity with time for polyethylene coating stored in desiccator at 23 ± 2°C

Melting temperature 245 C; melting time 5 min. in nitrogen atmosphere; heat-treatment at 150°C for 45 min. in nitrogen atmosphere.

1—cooling rate "A."   2—cooling rate "B."   3—cooling rate "C."

The second problem studied was the effect of the physical structure on the adhesive-cohesive strength of the bond. According to preliminary conclusions, in this case only peeling strength can be defined. The changes appearing in the physical structure were caused by cooling the specimens at different rates from the molten state. According to the conditions of the experiment, the degree of crystallisation and the size of spherulites in the PE coating changed in parallel with the cooling rate. The crystallinity, as well as the size of spherulites, increases with the decreasing rate of cooling. Characteristic spherulitic structures are represented in Figs. 10 and 11, while the percentages of crystallinity derived are in Table 4. The bond strength decreases very remarkably, approximately linearly with the decreasing rate of cooling (see Fig. 7). This may be brought about by a number of factors. As already mentioned above, the large size of spherulites, as well as the resulting viscoelastic properties of the coating, exercised a negative influence on the contact between the coating and the metal. At a higher cooling rate, there is the probability of a more favourable orientation of active groups of chains towards the steel surface and thus of a higher actual adhesive-cohesive strength.

Values of the percentage elongation, as well as the apparent modulus of elasticity, of the PE coatings prepared at extreme cooling rates, are given in Table 5. The lower extensibility of the coatings may be connected with the higher stress concentration in the areas where the coating separates from the steel base. A higher volume contraction, together with a higher modulus of elasticity, results in a higher stress in the coating/metal system and consequently also in the boundary layer. The appreciable differences in the internal stresses
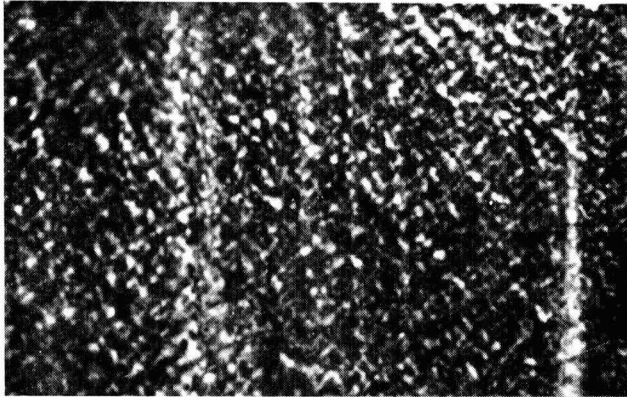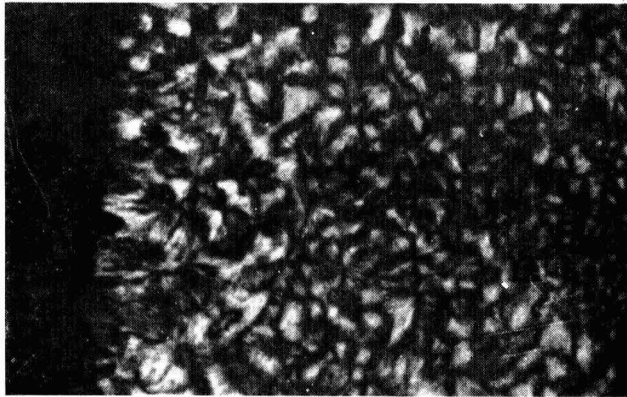
Fig. 10. Photomicrograph of the spherulite structure of polyethylene coating

Microscopic magnification 200×; photographic magnification 4×. Melting temperature 245 C; melting time 5 min. in nitrogen atmosphere; heat-treatment temperature 150°C, time 45 min. in nitrogen atmosphere, cooling rate "A."

Fig. 11. Photomicrograph of spherulitic structure of polyethylene coating

Microscopic magnification 200×; photographic magnification 4×. Melting: at 245°C for 5 min. in nitrogen atmosphere heat-treatment: at 150°C for 45 min. in nitrogen atmosphere; cooling rate "C."

occurring in the system PE coating/steel base has already been confirmed by orientation measurements, which are still under investigation. These stresses reduce the peeling-force. At the present time, it is not possible to determine more closely how the individual factors contribute to the peeling-force, particularly with respect to the adhesive-cohesive properties of the system. However, it is evident that the peeling strength of the system, which often comes into consideration when stress is exerted on the system, decreases appreciably with the increasing volume concentration and higher size of spherulites.

Fig. 12
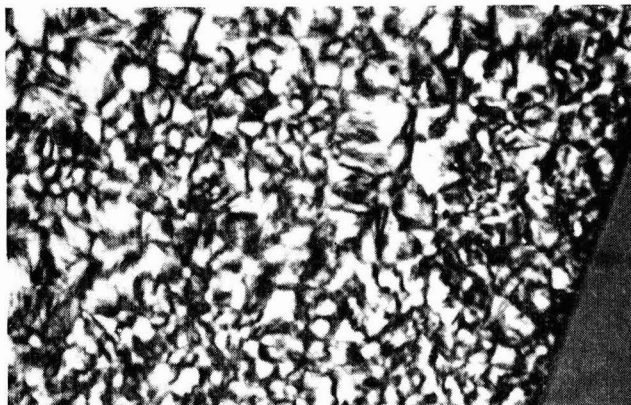
Fig. 13
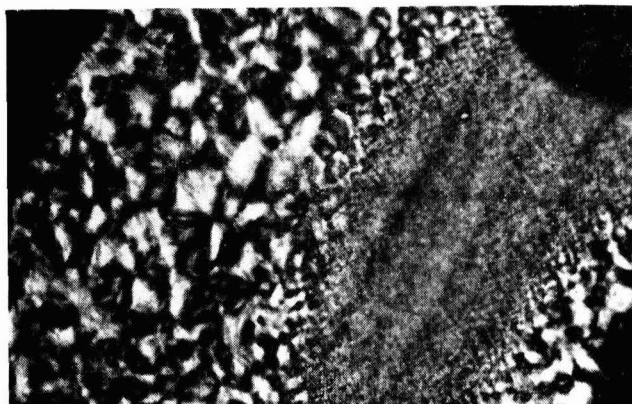
Fig. 12. Photomicrograph of spherulitic structure of polyethylene coating

Microscopic magnification 200×; photographic magnification 4×. Melting: at 245 C for 5 min. in nitrogen atmosphere heat-treatment: at 120 C for 45 min. in nitrogen atmosphere cooling rate "C."

Fig. 13. Photomicrograph of spherulitic structure of polyethylene coating

Microscopic magnification 200×; photographic magnification 4×. Melting: at 245 C for 5 min. in nitrogen atmosphere heat-treatment: at 150 C for 45 min. in nitrogen atmosphere; cooling rate "C."

Influence of the thermal oxidative conditions existing during the preparation of the coatings

References to the literature, indicating the favourable effect of oxidation on the adhesive properties of the polyethylene coatings, have already been cited in the Part I of the paper. It is of interest to determine the conditions required during preparations of the coating to give the optimum bond strength of the system. Therefore, an experiment was carried out to investigate more precisely the effect of the oxidation occurring simultaneously with the other changes during the coating preparation, and to determine the relationship between the bond strength of the coating/metal system and the complex of changes taking place in the coating. Care was taken to eliminate any effect due to changes in the coating.

Three groups of specimens were prepared. During the preparation of all specimens, the fusion temperature of the pulverised polyethylene was varied from 230 to 280°C, and the melting time was constant at 5 minutes.

The melting of polyethylene, as well as the heat-treatment of the resulting melt, were carried out in different ways for different groups of specimens. In the first group, both procedures (preparation and heat-treatment) were carried out in a nitrogen atmosphere, in the second group, the melting of pulverised polyethylene was carried out in air and the heat-treatment of the melt in nitrogen atmosphere, while the polyethylene powder employed for specimens of the third group was melted alternatively either in air or in nitrogen atmosphere and the resulting melt was then heat-treated in air. The heat-treatment temperature was fixed at 150°C, the treatment time was 45 minutes, the rate of cooling the system was 1°C.min⁻¹. If no irreversible changes took place in the coating during the preparation of specimens, the physical properties of the heat-treated coatings would be similar to each other and the adhesive-cohesive bond strength of the system could be evaluated explicitly.

Fig. 14 shows the dependence of peeling-force on the melting temperature of the polyethylene powder for all specimens. The changes of mechanical properties of the coating for the middle series of specimens are listed in Table 6. Table 7 gives the peeling-force values shown in Fig. 14, and also the specific gravities and colouration changes occurring in the coatings. The colouration was evaluated visually on the films used for infra-red spectroscopy. The structural changes that take place at temperatures of 260 and 280°C were further studied
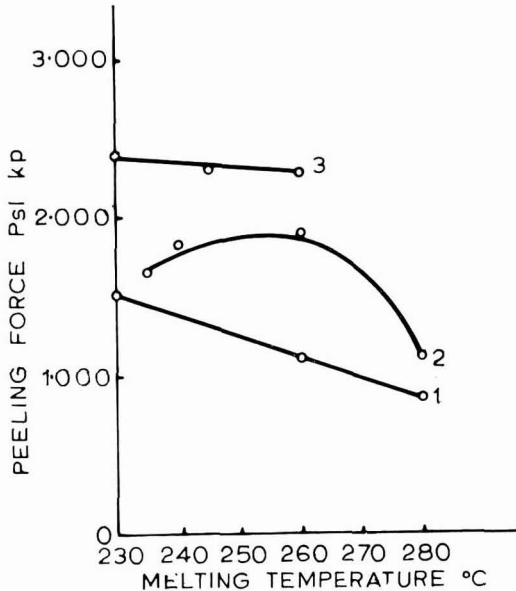
Fig. 14. Relationship between the peeling force on thermal oxidation conditions when preparing polyethylene coatings

1—specimens prepared and heat-treated in nitrogen atmosphere.
2—specimens prepared in air, heat-treated in nitrogen atmosphere.
3—specimens prepared either in air or nitrogen atmosphere, heat-treated in air.

Table 6

Effect of the thermal oxidation conditions on the mechanical properties of polyethylene coatings

Conditions of coating preparation:

melting time: 5 minutes in air
heat treatment: at 150°C for 45 minutes in nitrogen atmosphere,
cooling rate "C"

Temperature during preparation (°C)	Percentage elongation (%)	Yield stress (kp/cm²)	Stress at rupture (kp/cm²)	Apparent modulus of elasticity (kp/cm²)
225	157	89.5	84.0	1.6×10^3
245	93	92.0	81.0	1.73×10^3
265	60	94.5	81.0	2.33×10^3

Table

Effect of the thermaloxidative conditions on the peeling

Conditions of the coating preparation: Melting time 5 minutes;

Experiment No.	Preparation temperature	Values measured after preparation						
		in nitrogen atmosphere				in air		
		Peeling force (kp)	Variability	Specific gravity	Surface appearance	Peeling force (kp)	Variability	Specific gravity
1	230	—	—	—	—	1.81	10.3	0.9179
2	235	—	—	—	—	×	—	—
3	245	1.28	10.0	—	0	—	—	—
4	230	×	—	—	—	—	—	—
5	240	—	—	—	—	×	—	—
6	260	×	—	—	—	—	—	—
7	260	—	—	—	—	1.38	—	—
8	260	—	—	—	—	—	—	—
9	280	×	—	—	—	—	—	—
10	200	—	—	—	—	×	—	—

Comments: 0—Surface free of changes;   ×—Preparation of specimens under given conditions;
Ž1—Surface gets yellow

on cross-sections made through the coatings; the differences may be seen by comparing Figs. 12, 15 and 16. The results of infra-red spectroscopy measurements are given in Table 8. Changes of the relative carbonyl band absorption are very evident.

From the data listed in Table 6, it follows that the elongation at break decreases with rising temperature of the preparation in the range between 230 and 270°C, whilst the value of the modulus of elasticity of the coating increases considerably under the same temperature conditions.

These observations prove that irreversible changes take place in the coating at these temperatures. The thermal oxidation process of failure lies in the volatilisation of low-molecular components, and in the oxidation of the polyethylene, which may result even in a partial cross-linking. The volatilisation of the low molecular weight components can be seen visually during the preparation of the specimens, the results of the infra-red spectroscopy as well as the colouration of the surfaces of coatings give evidence of the extent of oxidation, whilst the start of the cross-linking process is indicated by the presence of bands having an amorphous appearance on the surface of the coatings (see Figs. 15 and 16). The specific gravity of the specimens increases as oxidation proceeds and as the volume changes. Irreversible volume changes reduce the measured peeling-force value. Since irreversible changes of the mechanical properties

7

strength of the system polyethylene coating/steel surface

Heat-treatment: Heat-treatment temperature 150°C;
Time 45 minutes; Cooling rate "C"

| | Values measured after heat-treatment | | | | | | | |
| | in nitrogen atmosphere | | | | in air | | | |
Surface appearance	Peeling force (kp)	Variability	Specific gravity	Surface appearance	Peeling force (kp)	Variability	Specific gravity	Surface appearance
0	—	—	—	—	2.4	9.7	0.9205	0
—	1.65	4.5	0.9197	0	—	—	—	—
—	—	—	—	—	2.33	5.1	0.9202	0
—	1.52	7.4	0.9187	0	—	—	—	—
—	1.83	11.3	0.9184	0	—	—	—	—
—	1.11	9.3	0.9192	Ž1	—	—	—	—
—	1.89	4.7	0.9200	Ž1	—	—	—	—
—	—	—	—	—	2.37	10.6	0.9203	Ž1
—	0.86	7.1	0.9208	Ž1	—	—	—	—
—	1.12	7.9	0.9207	Ž1	—	—	—	—

of the polyethylene coating also take place, caution must be exercised when determining the relationship between the oxidation of polyethylene and its adhesive-cohesive properties. The curve 1, plotted in Fig. 14, shows the development of unfavourable, irreversible changes which take place simultaneously

Fig. 15
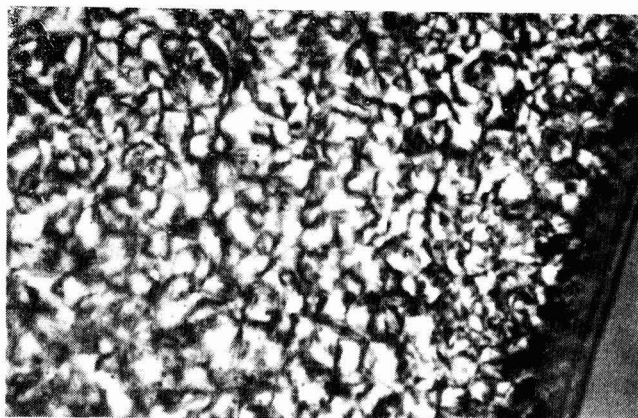
Fig. 16
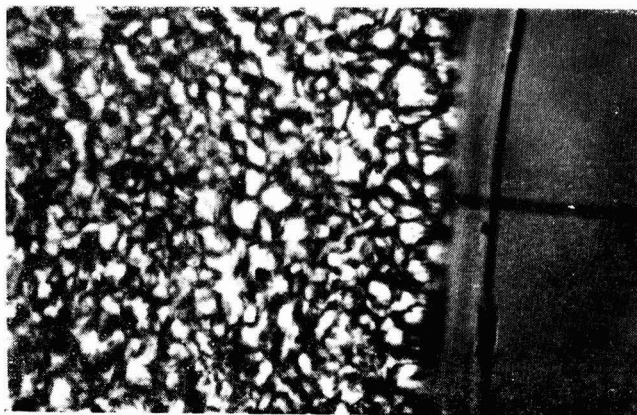
Fig. 15. Photomicrograph of spherulitic structure of polyethylene coating

Microscopic magnification $200\times$; photographic magnification $4\times$. Melting: at 260 C for 5 min. in air, heat-treatment: at 150 C for 45 min. in nitrogen atmosphere; cooling rate "C." Yellow coating surface.

Fig. 16. Photomicrograph of spherulitic structure of polyethylene coating

Microscopic magnification $200\times$; photographic magnification $4\times$. Melting: at 280 C for 5 min. in air, heat-treatment: at 150 C for 45 min. in nitrogen atmosphere; cooling rate "C."

with the temperature changes during the preparation process. Even after corresponding heat-treatment of the specimens prepared and heat-treated in a nitrogen atmosphere, the magnitude of the peeling force decreases. In circumstances where the specimens have been prepared in a normal air atmosphere, the course of temperature dependence alters markedly (see curve 2 in Fig. 14). At a certain temperature, the curve passes through the maximum. During the "heat-treatment," a further oxidation process takes place, caused by the presence of the oxygen absorbed during the preparation of the specimens. The favourable effect of the oxidation process is still more evident if the heat-treatment is carried out in air (see curve 3 in Fig. 14). From these results it follows that a

Table 8

Evaluation of the thermaloxidative changes of polyethylene coatings by infra-red spectroscopy

Experiment (see Table 7)	Characteristics of specimen			Average film thickness		Relative values of extinction					
	Conditions of preparation Atmosphere	°C	Heat-treatment Atmosphere	"P"	"V"	Band 1,720cm⁻¹ "P"	"V"	Band 1,450cm⁻¹ "P"	"V"	Band 876cm⁻¹ "P"	"V"
				m							
0	reference			120		1.2		92		3	
1	air	230	air	183	187	1.0	1.0	—	—	1	3
1	air	230	nitrogen	140	120	14.0	1.0	87	19	—	2
4	nitrogen	230	nitrogen	135	140	1.1	1.0	70	64	2	2
5	air	240	nitrogen	132	133	—	1.0	—	—	—	—
6	nitrogen	260	nitrogen	156	140	28.0	2.1	56	70	2	2
7	air	260	nitrogen	135	155	29.6	2.0	71	62	—	2
8	air	260	air	210	170	43.0	2.4	36	56	—	3
9	nitrogen	280	nitrogen	133	155	44.0	2.9	61	65	—	3
10	nitrogen	280	air	133	118	45.0	4.0	—	—	—	—

temperature of 260°C represents the optimum for the preparation of the given polymer and time of melting-through. Temperatures above this give rise to a deterioration in the PE coating, whatever the conditions of preparation. Surface yellowing and a band without spherulites may be observed near to the surface (see Table 7 and Fig. 15). At a temperature of 280°C, the boundary layer, even after the heat-treatment process, shows an undulating edge (see Fig. 16).

These microscopic results may be compared, using infra-red spectroscopy, with the changes in chemical structure.

In all specimens which have been both prepared and heat-treated in nitrogen atmosphere (Fig. 14, curve 1), the measured peeling force decreases with the change in the temperature of preparation. The amount of carbonyl groups increases near the coating surface and even slightly inside the coating. The surface at the same time becomes yellow and wrinkled. At the temperatures used, the oxidation process occurs during the specimen's preparation, and the decrease of the peeling force is evidently caused by long term volume changes, as well as by a change in the viscoelastic properties, Both these factors cause an increase of stress in the interfacial surface, and stress concentration in the area of the relaxation of the bond between the coating and metal also increases. In the case where specimens prepared in nitrogen atmosphere are heat-treated in air, almost entire equalisation of the peeling-force temperature relationship occurs (see the curve 3 in Fig. 14). The oxidation changes occurring during the heat-treatment process manifest themselves positively and compensate for the unfavourable effect of the physical changes discussed above. Curve 2, representing the course of peeling force changes occurring simultaneously with the changes of temperature in specimens prepared in air and heat-treated in nitrogen, lies somewhere between curves 1 and 3. Its position and shape prove again that the favourable oxidation changes take place during the heat-treatment process. At higher temperatures, above 260°C, however, the unfavourable changes predominate. If the relative amounts of carbonyl groups estimated both in surface and interior areas of coatings, as shown by curves 1 and 2, are compared, it is found that although they are identical for 230, 235 and 260°C (see Table 8), the peeling force shown by curve 2 is much higher. From this observation it follows that the changes in the amount of carbonyl groups alone do not indicate favourable oxidation changes. The double bond is more sensitive to oxidation than the methyl groups. However, the measurement of the changes occurring in the number of double bonds determined by the infra-red spectroscopy is less sensitive. Because of the similar character of the surface oxidation of the specimen compared, the sum of $P + V$ values (see Part I) will have to be used. For specimens plotted in curve 1 the sum equals 4, for specimens plotted in curve 2 the sum is lower and equals 1 to 2. The higher strength of the bond may be thus attributed to oxidation which occurs at the temperature of the heat-treatment process and leads to a degree of oxidation.

From the tests carried out as mentioned above, it follows that oxidation improves the adhesive-cohesive properties of polyethylene coatings. When characterising the oxidation, it is, however, necessary to consider all aspects of the oxidation process. The time dependence of oxygen diffusion through the coating as well as the oxidation occurring inside the coating are very important

factors. Therefore, it is much more efficient to carry out oxidation at lower temperatures but for longer periods, since under such conditions no simultaneous, unfavourable, thermal oxidation, changes take place.

Conclusions

It follows from the experimental work and analyses carried out that, for the current polyethylene coating/steel base system, only the adhesive-cohesive properties of the polyethylene coating can be determined. The method of stepwise peeling of the coating does not permit the determination of a precisely defined adhesive-cohesive constant quantity, only the relative bond strength value of the system PE coating-metal for the given type of strain.

The use of the methods described enables an evaluation of the effects of the steel base properties and of the physicochemical structure of the coating on the adhesive-cohesive strength of the bond.

The bond strength increases with the extent of the specific surface of the steel base; however, if the steel surface shows considerable unevennesses, this proportionality is disturbed. This is probably due to the fact that the coating does not fill up deep hollows. The marked effect of the polyethylene oxidation on the adhesive-cohesive properties of polyethylene has been confirmed. However, the number of carbonyl groups present must not be regarded as an unfailing indication of the significant oxidation changes which take part in the increase of the bond strength. The oxidation occurs under such conditions that simultaneous irreversible physico-mechanical changes in the polyethylene coating can occur. It has become evident that coatings exhibiting a fine spherulitic structure and the resulting physico-mechanical properties contribute to the attainment of the best contact between the PE coating and the steel. When the modulus of elasticity of the PE coating is reduced, which results in a reduction of the internal stress in the system, the measured strength of the bond significantly increases.

From the relationship established, it follows that the maximum bond strength of the coating will be obtained on a steel base with a large specific surface, which, however, should not show too great roughness. The coatings have to be subjected to a sufficient melting-through carried out in an oxidising atmosphere at temperatures which do not allow unfavourable physico-mechanical changes in the coating. In addition, the system must be brought to the solid state by rapid cooling.

Acknowledgment

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The formulation of fungus-resistant paints: IX. Influence of the primer and of pigments causing chalking

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Summary

It is shown that a top coat over a commercial linseed oil primer has a lower resistance to mould than one over a latex primer. Several modified formulations of the primer were investigated and the most successful in counteracting this tendency was the one containing copper 8-hydroxyquinolate.

The widespread belief that chalking is beneficial in keeping a painted surface free of mould is shown to be mistaken.

Key words

Properties, characteristics and conditions primarily associated with dried or cured films

    chalking
    fungus

Types and classes of coating

    latex coating
    oil paint
    primer

Biologically active agents

    copper 8-hydroxyquinolate

Binders—oils, etc.

    linseed oil

La mise au point des formules de peintures résistantes á végétation mycélienne. 9ème. Partie. L'influence du primaire et des pigments farinants

Résumé

On démontre dans le cas d'une couche de finition appliquée sur un primaire de commerce à base d'huile de lin que la résistance à végétation mycélienne est plus faible que celle d'une couche de la même peinture appliquée sur une peinture-émulsion. On a investigé plusieurs modifications de la formule du primaire, et l'on a trouvé que la plus éfficace à cet égard contient de 8-hydroxyquinolate de cuivre.

On démontre fausse l'opinion répandue qui tient le farinage avantageux en maintenant une surface peinte exempte de moisissure.

Rezepturaufbau für Pizanwuchsbeständige Anstrichfarben IX—Einfluss von Primer und Abkreidenden Pigmenten

Zusammenfassung

Es wird aufgezeigt, dass eine Überzugsfarbe über einem handelsüblichen Primer auf Leinölbasis weniger gegen Pilzbefall beständig ist, als eine über einem Latexprimer aufgetragene. Verschiedene Primerrezepte wurden geprüft. Dabei erwies sich als dieser Neigung am besten entgegenarbeitend eine, die Kupfer-8-Hydroxyquinolat enthielt.

Der weitverbreitete Glaube, dass Kreiden dazu beitrüge, Anstrichfarben von Pilzwuchs freizuhalten, wird als irrig aufgezeigt.

Формуляция красок устойчивых против плесени
IX-Влияние грунтовки и пигментов вызывающих известкование

Резюме

Показано что наружное покрытие над грунтовкой промышленного льняного масла, менее устойчиво против плесени чем слой поверх латексной грунтовки. Исследовалось несколько модифицированных формуляций грунтовок и наиболее успешной грунтовкой противодействующей этой тенденции оказалась грунтовка содержащая 8-гидроксихинолат меди.

Показано что широкораспространенное мнение о том что известкование содействует в освобождении окрашенной поверхности от плесени, является ошибочным.

Introduction

In previous publications, the effect of fungicides and fungistatic agents on the fungus resistance of paints was studied[1]. The method used at the Division of Building Research for assessing the effectiveness of fungicides includes, apart from exposure tests, determination of the stability of the additives in the paint film on exposure. In this way the observations can be better interpreted, and a more rational estimate can be made of the conditions under which a given fungicide is likely to be effective and for how long this will be the case[1].

However, the composition of a top coat does not exclusively determine its resistance to mould, which is well illustrated by a case in Cairns, North Queensland. Of two houses, both painted with a gloss latex paint, one showed prolific growth of mould and the other had none. The latter was a repaint on a previously decorated surface, whereas the former was a new house which had been painted with a linseed oil-based primer before applying the gloss latex paint. It was natural to suspect that the primer was the cause of the trouble, and, although at least some paint technologists believe that linseed oil primers would lower the resistance of the top coat to fungus growth, no systematic investigation to demonstrate the validity or otherwise of this view has been published.

A widespread belief amongst paint technologists is that fungus resistance is higher on a chalking surface, but again no systematic work appears to have been carried out on this point. This paper deals with both these questions.

Experimental

Asbestos cement panels 12in × 6in (30cm × 15cm) were coated with one of the five primer formulations used in this investigation, and were then given two coats of a latex paint either pigmented with rutile titanium dioxide only or with rutile titanium dioxide and zinc oxide.

For the experiments on the influence of chalking on the growth of mould, the unprimed asbestos cement panels received two coats of one of the following paint formulations:

(a) containing anatase titanium dioxide to cause copious chalking,

(b) with rutile titanium dioxide for minimum chalking,

(c) with rutile titanium dioxide and zinc oxide; formulated for fungus resistance.

The panels were exposed at 45° facing 31° east of north at Lae, New Guinea. The percentage area covered by mould (*C*) and its intensity (*I*) on a scale 9

Table 1

Assessment of mould growth on paint films over different primers exposed outdoors at Lae: upper side of panels

Paint	Primer	Replicates	Exposure															
			7 months		10 months		12 months		15 months		18 months		22 months		25 months		28 months	
			I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
L/r TiO₂	1	1, 2, 3	2	100	4	100	4	100										
	2	1, 2, 3	4	100	6	100	6	100										
	3	1, 2, 3	3	100	6	100	6	100										
	4	1, 2, 3	9	5	6	100	6	100										
	5	1, 2, 3	1	95	1	100	1	100										
L/r TiO₂.ZnO	1	1, 2, 3	0	100	1	100	1-3	100	2-3	100	2-3	100	2-3	100	2-4	100	4	100
	2	1, 2, 3	0	100	1	100	1	100	2-4	100	2-4	100	2-4	100	2-4	100	1-3	100
	3	1, 2, 3	1	100	1	100	1	100	2-3	100	2-3	100	2-4	100	2-4	100	1-3	100
	4	1, 2, 3	0	100	1	100	1-3	100	1	100	1	100	1	100	1	100	1	100
	5	1, 2, 3	0	100	1	100	1	100	2-4	100	2-4	100	3-4	100	2-4	100	3	100

C = Percentage area covered by colour intensity I

I = Intensity of colour according to scale 9 (black) and 0 (white)

I = 0 and C = 100 means that the panel is free of mould

(black) to 0 (white) were assessed visually at intervals of 3 or 4 months, and these assessments are recorded in Tables 1-3. The panels in Fig. 1 illustrate the appearance of surfaces with various combinations of intensity and coverage.

Details of the primer and paint formulations used are given in the Appendix.

Fig. 1

Fig. 1. Examples of assessment of mould growth
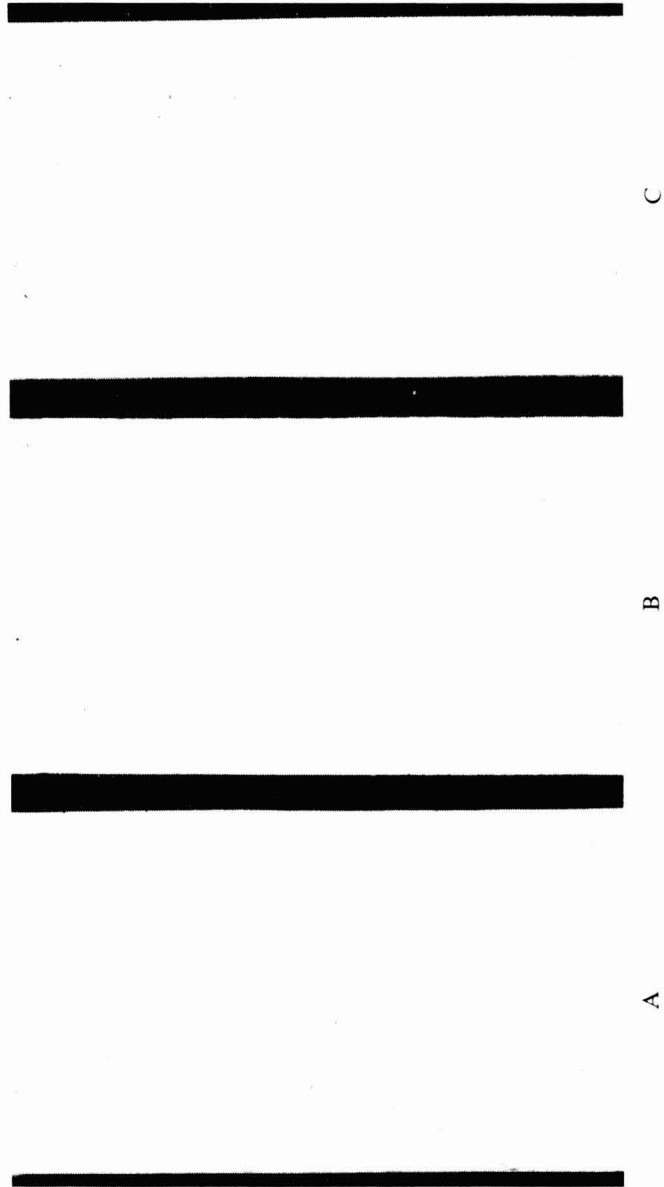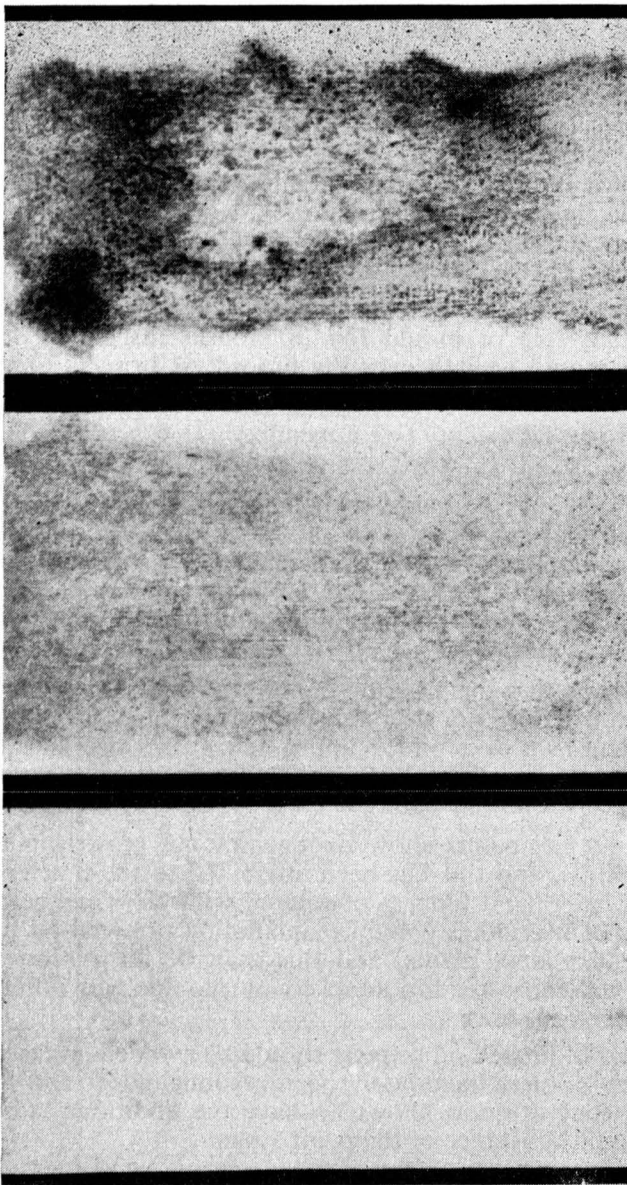
A. I = 0, C = 100   B. I = 1, C = 100   C. I = 2, C = 100   D. I = 4, C = 100
E. I = 6, C = 100   D. I = 8, C = 80   I = 1, C = 20

Discussion

Influence of primer on mould growth on the finishing coat

(a) Finishing coat L/r TiO$_2$. (see Appendix)

On the upper side (Table 1) all panels which had been primed with one of the linseed oil primer combinations (nos. 1 to 4) showed appreciable mould

growth after 7 months, but those primed with the latex primer (no. 5) were practically free of mould for 12 months and then showed somewhat less mould than the others.

Panels treated with primer no. 1 (which contains zinc oxide) seemed to have a little less mould growth than those primed with other linseed oil preparations, but the difference was too small to be important. However, it should be pointed out that the zinc oxide in primer no. 1 is a commercial product which has been shown to be of little value as a mould inhibitor[2]. It would therefore be of interest to repeat the experiments with a type of zinc oxide which is known to be effective.

The pattern and extent of mould growth on the under side of the panels (Table 2) were similar to that on the upper side, but the panels with no. 5 (latex) primer were practically free of mould for 28 months instead of 12 months. The intensity of the mould growth over the linseed oil primers appears to be higher in all cases on the under side than on the upper side.

(b) Finishing coat L/r TiO_2. ZnO (see appendix)

The upper side of panels treated with linseed oil formulations 1, 2, and 4 (Table 1) showed appreciable mould growth after from 12 to 15 months, whereas those which had been primed with the latex composition (no. 5) or the primer containing copper 8-hydroxyquinolate (no. 3) were practically free of mould for 25 months and even later. On the under side (Table 2), the panels with primer no. 5 showed very little mould growth for 15 months, whereas in all other cases there was strong growth after seven months.

It is important to note that the addition of copper 8-hydroxyquinolate (CuH) to the linseed oil primer does not decrease the growth of mould on the under side to the same extent as it does on the upper side. It has also been shown for gloss and flat enamel paints that CuH is effective on outside exposure only on the side which receives strong light[3].

As a rule, gloss enamel paints show stronger mould growth in the humid tropics than latex paints, and this has been attributed to the inherently higher mould resistance of latex paint films as compared with gloss enamel films. The present experiments offer another possible explanation. Linseed oil primers are not usually used under latex paints, and this may be the reason why gloss enamel paint films are more readily attacked by mould, and not because of some inherently lower resistance.

In any case, the use of linseed oil primers should be avoided, at least in humid tropical areas. Latex primers have lately been recommended, and apart from more rapid drying, they are now shown to have the additional advantage of not lowering the mould resistance of the paint system.

If for some reason it is not desired to use latex-based primers, the linseed oil primer could be modified to counteract the tendency to impart increased mould sensitivity to the paint system. The addition of CuH is one way, although it is not a complete answer. Changing the formulation from raw to refined linseed oil and using the type of zinc oxide that inhibits mould are two other possibilities worth considering.

The complexity of the problem of formulating fungus-resistant paints is highlighted by the trials with CuH. In the experiments reported here, it was

Table 2

Assessment of mould growth on paint films over different primers exposed outdoors at Lae: under side of panels

Paint	Primer	Replicates	Exposure															
			7 months		10 months		12 months		15 months		18 months		22 months		25 months		28 months	
			I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
L/r TiO₂	1	1, 2, 3	5	30	5	70	5	70										
	2	1, 2, 3	2	70	2	30	2	30										
	3	1, 2, 3	5-7	100	6-8	100	7-9	100										
	4	1, 2, 3	6	100	6	50	8	80										
	5	1, 2, 3	5	50	8	50	2	20										
L/r TiO₂ ZnO	1	1, 2, 3	5-9	100	1	100	1	100	1	100	1	100	1	100	1	100	1-2	100
	2	1, 2, 3	7	30	8	90	9	50	9	90	9	90	9	90	9	90	9	90
			3	70	5	10	5	10	5	10	5	10			3	10	3	10
	3	1, 2, 3	9	50	8	90	9	90	7	90	7	90	5-6	100	5-6	100	5-6	100
			3	50	5	10	5	10	5	10	5	10						
	4	1, 2, 3	9	30	4	80	9	90	9	90	4	90	9	90	9	90	9	90
			4	70	5	20	5	10	5	10	5	10	3	10	3	10	3	10
	5	1, 2, 3	1	100	8	80	8	90	8	90	8	100	7-8	100	7-8	100	7	90
					4	20	5	10	2	10	3	100	2	100	2	100	5	10
							1	100	1-2	100							2	100

C = Percentage area covered by colour intensity I
I = Intensity of colour according to scale 9 (black) and 0 (white)
I = 0 and C = 100 means that the panel is free of mould

Table 3

Comparison of mould growth on chalking paint films with non-chalking ones exposed outdoors at Lae

Side of panel	Paint	Replicates	Exposure															
			3 months		7 months		9 months		12 months		16 months		19 months		21 months		24 months	
			I	C	I	C	I	C	I	C	I	C	I	C	I	C	I	C
Upper	L/r TiO₂.ZnO	1, 2, 3, 4	0	100	0	100	0	100	0	100	0	100	9/1	5/95	4	50	4-5	100
	L/a TiO₂		0	100	4-5	10	2-3	100	2-3	100	3	100	3	100	3	100	3	100
	L/r TiO₂		0	100	1-2	100	2-3	100	1-2	100	1	100	2	100	2-3	100	2-3	100
Under	L/r TiO₂.ZnO		0	100	0	100	2-3	100	2-3	100	2-3	100	2	95	3	100	5/1	20/80
	L/a TiO₂		1-2	20	1-5	100	3-5	100	3-5	100	5	100	5	100	5	100	5-6	100
	L/r TiO₂		2-3	40	2-3	40	1-2	50	1	50	1	50	1	100	1	100	7/7	40/5

C = Percentage area covered by colour intensity I

I = Intensity of colour according to scale 9 (black) and 0 (white)

I = 0 and C = 100 means that the panel is free of mould

found that this compound, when incorporated into the linseed oil primer, increased the mould resistance of the top coat only on the upper side of the panels, and only in the finishing coat containing zinc oxide (Table 1, primer 3). No explanation for this can be given, but it suggests another possibility for formulating a mould-resistant paint system. The paint used here contains approximately 40 per cent by weight of zinc oxide, and consequently chalks badly on outside exposure. If less pigment were used in the formulation, its mould resistance would be reduced[2], and it would be reasonable to consider whether a paint system containing CuH in the undercoat and only small quantities of zinc oxide in the top coat would still show an increased fungus resistance.

Influence of a chalking formulation on mould resistance

It is clear from an examination of the results in Table 3 that the paint formulated with anatase titanium dioxide and which chalks readily is not more mould resistant than the paints formulated with rutile titanium dioxide, which are less prone to chalking.

Conclusions

The use of linseed oil primer should be avoided in humid tropical areas because of its tendency to decrease the mould resistance of the top coat. A latex-based primer does not increase this tendency, and from this point of view is the most satisfactory at the present time. Of the modifications of the linseed oil primer which were tried, the addition of copper 8-hydroxyquinolate gave a primer which compared well with the latex-based primer for exposed outdoor use. Contrary to the widespread belief, chalking in itself does not decrease the tendency for mould to grow.

Work to develop a suitable linseed oil primer which does not promote mould growth would appear to be worthwhile, and suggestions in this direction are made.

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Appendix

Formulations

Primer no. 1 Raw linseed oil .... 500 parts by weight
    Zinc oxide .... 400 ,, ,, ,,
    Rutile titanium dioxide 200 ,, ,, ,,
    Extenders .... 556 ,, ,, ,,
    Driers
    PVC 40 per cent

Primer no. 2 Zinc oxide pigment replaced by same volume of rutile titanium dioxide

Primer no. 3 Same as (2) with 1.5 per cent copper 8-hydroxyquinolate added

Primer no. 4 Same as (2) with 1.5 per cent N-trichloromethylthio-phthalimide
　　　　　　　added

Primer no. 5 100 per cent acrylic latex　582 parts by weight
　　　　　　　Rutile titanium dioxide　294　,,　　　,,　　,,
　　　　　　　Extenders　　　　　　　123　,,　　　.,　　,,
　　　　　　　Wetting agents
　　　　　　　PVC 33 per cent

Finishing coats

Latex resin—vinyl acetate acrylate copolymer
PVC—40 per cent
L/r TiO_2—Pigment rutile titanium dioxide
L/r TiO_2. ZnO—Pigment rutile titanium dioxide and zinc oxide, 1:1 by vol.
L/a TiO_2—Pigment anatase titanium dioxide

Application of silicas and silicates in the paint industry*

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Summary

The article sets out to discuss the manufacturing processes of synthetic silicic acids and silicates, together with their application in the surface coating industry.

As a result of electron microscopic tests and graphic presentation the influence of the dispersion of pyrogenic colloidal silicic acid and its efficiency as a thixotropic and anti-sedimentation agent is demonstrated. Similarly, the effect of polarity of various media on silicic acid is described. By a special process of manufacture, a hydrophobic type of silicic acid can be produced, and its use as an anti-corrosive agent in primers and marine paints is shown. Furthermore, the matting properties of special silicic acids are discussed, as well as those of aluminium silicates which are used to improve the hiding power and brilliancy of white and coloured emulsion paint systems.

Keywords

Extender pigments	*Process and methods primarily associated with analysis, measurement and testing*
aluminium silicate	electron microscopy
fumed silica	
precipitated silica	
pyrogenic silica	

Applications des silices et des silicates à l'industrie de peintures

Résumé

L'exposé a pour but la discussion des procédés de fabrication des acides siliciques et des silicates également synthétiques, ainsi que leur application à l'industrie de peintures.

Au moyens des examens par microscope électronique et à l'aide des dessins graphiques on démontre l'influence qu'exerce le niveau de dispersion de l'acide silicique colloïdal et pyrogéné, et également son efficacité en tant qu'un agent thixotrope ou anti-déposant. De même façon, on décrit l'effet exercé par la polarité de divers liants sur l'acide silicique. On peut produire au moyens d'un procédé spécial de fabrication un type hydrophobe de l'acide silicique, et l'on démontre son utilisation en tant qu'un agent anti-corrosif en primaires et en peintures marines. D'ailleurs on discute les propriétés de mattage des qualités spéciales des acides siliciques, ainsi que celles des silicates d'aluminium que l'on emploie pour augmenter le pouvoir couvrant et le brillant des peintures-émulsions blanches ou colorées.

Einsatz von Kieselsäureanhydrid und Silikaten in der Lackindustrie

Zusammenfassung

Der Zweck dieses Artikels ist, die Herstellungsverfahren künstlicher Kieselsäuren und Silikate, ebenso wie deren Anwendung in der Lackindustrie zu besprechen.

Der Einfluss der Dispersion pyrogener, kolloidaler Kieselsäure und ihre Wirksamkeit als thixotropes und absetzenverhütendes Mittel wird, unterstützt von elektronenmikroskopischen Prüfungen und graphischen Darstellungen, aufgezeigt. In gleicher Weise wird der Einfluss der Polarität verschiedener Bindemittel auf Kieselsäure beschrieben. Ein hydrophober Typ der Kieselsäure kann mit Hilfe eines Spezialverfahrens hergestellt werden. Sein Einsatz als Rostschutzmittel in Primern und Schiffsfarben wird aufgezeigt. Es werden weiterhin die Eigenschaften spezieller Kieselsäuren mattierend zu wirken, ebenso wie die der Aluminiumsilikate, welche zur Verbesserung der Deckkraft und der Brillanz von weissen und farbigen Emulsionsfarbensystemen verwandt werden, besprochen.

Применение окисей кремния и силикатов в красочной промышленности

Резюме

Статья обсуждает производственные процессы синтетических кремневых кислот и силикатов и их применение в производстве поверхностных покрытий.

При помощи электрономикроскопических испытаний и графического изображения демонстрируется влияние дисперсии пирогенной коллоидной кремневой кислоты и ее продуктивность в качестве тиксотропной и противоосадочной среды. Описывается также влияние полярности различных сред на кремневую кислоту. При помощи специального производственного процесса можно получить гидрофобный тип кремневой кислоты и описывается ее применение в качестве противокоррозийного средства в грунтовках и судовых красках. Далее обсуждаются матовые свойства специальных кремневых кислот и силикатов алюминия, которые применяются для улучшения укрывистости и блеска белых и цветных эмульсионных красочных систем.

Introduction

The use of colloidal silicas in the coatings industry has steadily increased over several decades. Fumed colloidal silicas have been used to a varying extent for more than 15 years in viscosity control, for imparting thixotropy, for matting and to prevent settling of pigments. Fumed silicas have found application in all types of surface coating finishes. Specialised forms of silica have been developed for satisfying specific matting requirements of manufacture. Having a particle size range of 1-15 microns depending on the type of product, they can no longer be classified as colloidal silicas. On the other hand, the particles up to 15 microns are secondary particles and consist of small primary particles in the colloidal range of 1 to 10×10^{-6} metres. These products are far more efficient in meeting matting requirements than the fumed colloidal types.

Production methods and properties of fumed colloidal silicas

Chemically, fumed silica is pure silicon dioxide, obtained by burning silicon tetrachloride in an oxy-hydrogen flame. Physically, it is a blue-white powder and, unlike precipitated silicas, its loosely agglomerated, spherical particles have no internal surface. Ultimate particle diameter ranges from 5 mμ to 35 mμ, as can be seen in Figs. 1 and 2.
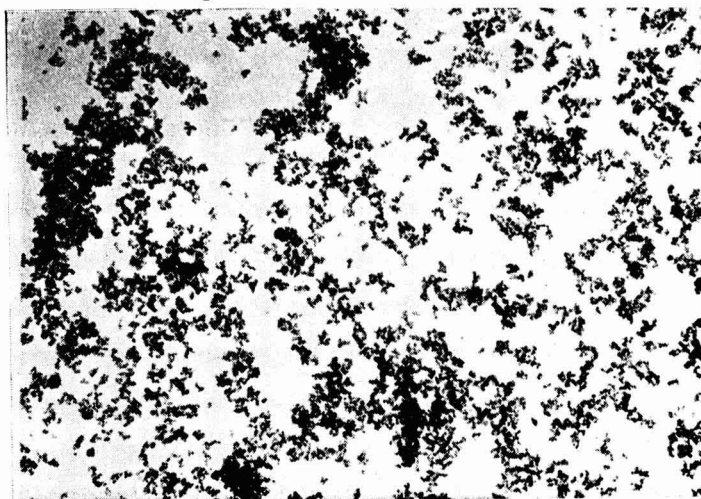
Fig. 1. Fumed silica with a particle size of 5-10 mμ
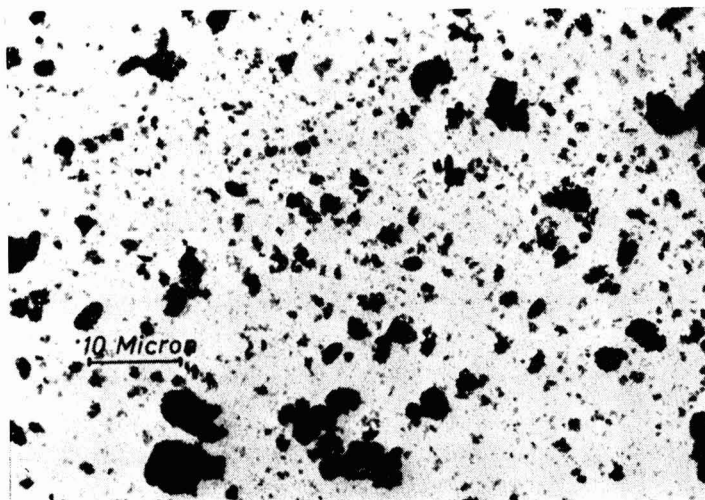
Fig. 2. Fumed silica with a particle size of 35 mμ

Also present on their surfaces are uniformly distributed silanol groups. These groups are strongly attracted to each other and allow the particles to form chains by hydrogen bonding. The chains progressively link together to form a three-dimensional structure, which is responsible for many of the functions performed by the silica.

Thixotropy and suspension

The three-dimensional chain structure of the silica particles accounts for their ability to increase the viscosity of liquid systems. As the silanol groups on one particle hydrogen-bond with their counterparts on others, liquid is entrapped and immobilised. Although the bonds are weak, application of shear will break them, allowing good flow, but the chains reform again after cessation of the shear force. Systems exhibiting these characteristics are called "thixotropic."

Colloidal silicas are able to impart the necessary thixotropy to coatings which are to be applied in thick layers. Thixotropic primers and coatings can be applied at difficult places, e.g. sharp edges, regardless of the method of application. Another function of thixotropy is its ability to keep pigments in suspension.

Suspension characteristics associated with fumed silicas also originate with the formation of three-dimensional chains. These chains weave an extensive network throughout a system, and it is this closely knit structure that supports particles of pigment and extender, causes thixotropy, and immobilises pigments to prevent floating during the drying stage.

The extent of the particle network can be visualised by considering the fact that one gram contains 3×10^{17} particles. Assuming a particle diameter of 20 μm, the particles from one gram, if lined up, would cover a distance of 6,000,000 Km. Owing to this extremely fine particle size, gloss is not affected,
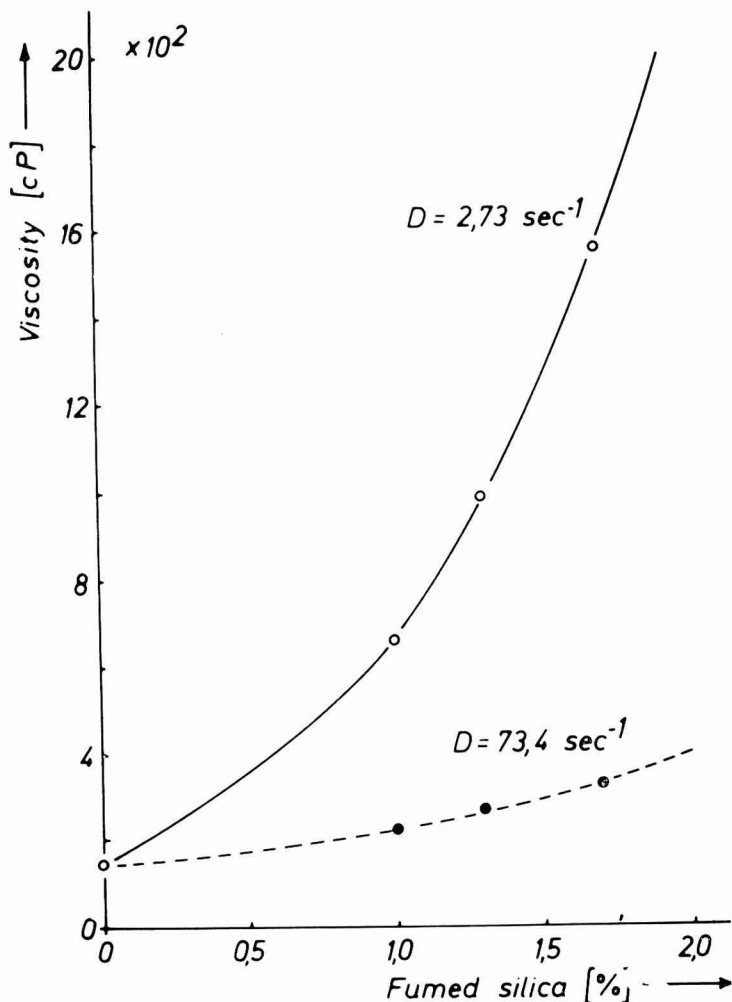
Fig. 3. Typical hysteresis curve for fumed silica

even with the relatively high concentrations, as long as the dispersion and shear are sufficient.

Dispersion

Owing to its strong shearing action, the triple roll mill is, of course, an efficient device for the dispersion of the silica. In this case, the best results are obtained with a master batch containing 8 to 10 per cent of the silica. It is necessary to let down the master batch since during storage a marked viscosity increase will occur, which will render the product unmanageable later. An attritor mill has also given excellent results when manufacturing master batches, with an optimum fumed silica content of 5 per cent. Pastes of this concentration can also be dispersed in a ball mill, but when a sand mill is used an optimal concentration of 3 per cent is recommended.
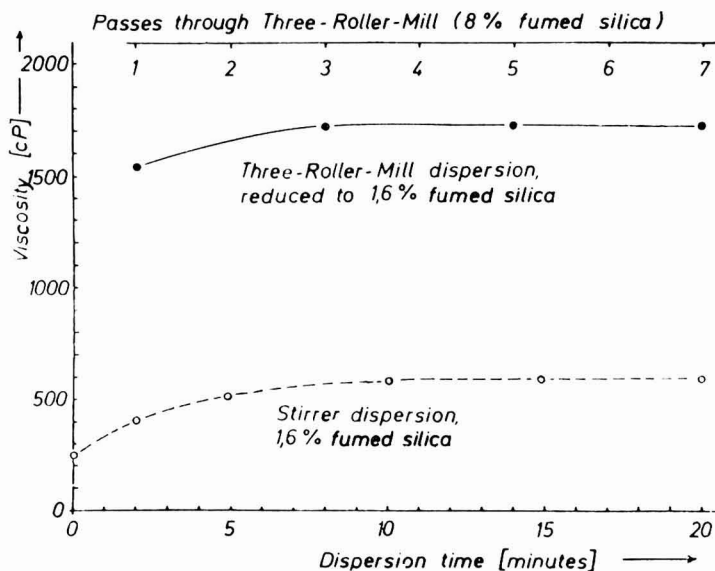
Fig. 4. Comparison of the efficiency of a high speed stirrer with that of a triple-roll mill

Even with a longer dispersion period, the use of a high speed stirrer is far less efficient than a triple-roll mill, or the other aforementioned types of equipment, because, normally, a higher addition of silica is needed to obtain the same degree of thixotropy realised with this equipment.

In general, therefore, the preparation of a master batch is recommended when developing highly thixotropic coatings. When the silica is intended to suspend pigments in a vehicle, it should be dispersed together with the pigments instead of master batching. Concentrations are lower than those needed to achieve a thixotropic system, and approximately 2-3 per cent based on the weight of the pigment and fillers is sufficient. Any of the aforementioned types of equipment can be used for this application.

Influence of polar systems on thixotropy

Viscosity and thixotropy are more pronounced when fumed silica is added to a non-polar system than to a polar one, because in the former case hydrogen bonding must take place between the silica particles exclusively. If the system contains other polar groups, such as hydroxyl groups, the silanol groups on the silica surface can bond indiscriminately with polar groups in the solvent or vehicle. Such interactions interrupt the formation of the silica chain structure, thus reducing the degree of thixotropy, as can be seen in Fig. 5.

Mineral spirits, for example, which are non-polar can be gelled by 2 per cent of fumed silica, but ethyl alcohol, a polar liquid, requires 20 per cent. In practice, of course, mixtures of polar and non-polar solvents are usual. Generally, a slightly higher concentration will produce a sufficient degree of thixotropy. Furthermore, it has been found that an intimate blend of colloidal silica and colloidal alumina manufactured by the pyrogenic process, with a silica content
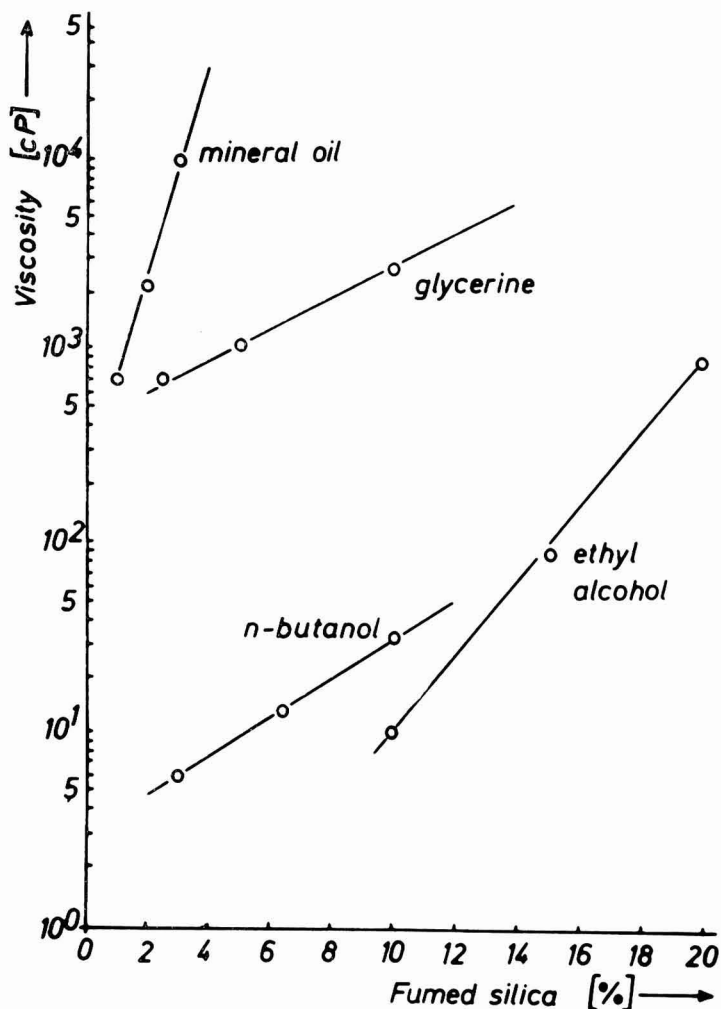
Fig. 5. Viscosity of fumed silica in different liquids

of 84 per cent, is a very effective viscosity control agent in aqueous and polar media.

Hydrophobic colloidal silica

The silanol groups which are present on the surface of fumed silica cause it to be hydrophilic in nature. If the silanol groups are replaced by methyl groups during the manufacturing process, a hydrophobic product with markedly different properties is obtained. For example, the hydrophobic silica cannot impart a high degree of thixotropy because of the absence of most of the silanol groups, and, therefore, it has a reduced tendency to form hydrogen bonds. This hydrophobic silica is more efficient in increasing the moisture resistance of coating systems, which is of special importance for all types of anti-corrosive

introduction to paint technology

second edition with additional chapter

The sales of this Association publication now exceed 13,000, and because of continuing high sales of the second edition, and the need for a work of reference to be constantly abreast of the latest developments in its field, the Council of the Oil and Colour Chemists' Association has authorised the addition of an eleventh chapter to the 'Introduction to Paint Technology.' Entitled 'Recent Developments,' the Chapter incorporates up-to-date information on the latest advances in the technology of the paint and allied industries.

This addition will help the 'Introduction to Paint Technology' to maintain its position as an invaluable aid to young entrants into the industries and to marketing and other personnel requiring a basic knowledge of the principles and techniques of surface coating production and application.

new chapter

The new chapter is subdivided to three sections

resins and media

Including polyester, epoxy, polyurethane resins and developments in water based paints, vinylics, etc.

application techniques

Including electrodeposition, powder coatings, strip-coating, aerosol spraying.

instrumental testing and control methods

Including colour measurement, viscometers, brushability, hardness, film thickness, weatherometers, and use of computers.

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coatings. The improved durability arising from the use of this hydrophobic silica is readily apparent. Primary areas of application are anti-corrosive primers and marine paints. In addition to its anti-corrosive properties and its function as a suspending agent, remarkable degassing effects have been noted in zinc rich primers.

Matting agents

The matting effect occurs through a controlled submicroscopic roughening of the coating surface. Any desired degree of matting can be achieved by choosing the particle size of the agent, its degree of dispersion and its concentration. Naturally, the roughness of the coating surface can vary only within certain limits. Thus, the disturbance of the coating surface must not be visible to the naked eye. As in many problems with surface coatings, a compromise must be found.

Figs. 6, 7, 8 illustrate the conditions on the lacquer surface; a pigmented polyurethane lacquer is shown in three gloss stages, and in oblique and direct light. In oblique light, the structures of the surfaces are readily detected by the contrast of light and shadow, while under direct illumination the distribution of the matting agent in the film is visible. For matting purposes, a special fumed silica with more strongly agglomerated primary particles should be selected, as this makes the silica more stable to over dispersion. It should be considered that the thickening effect of fumed silicas in general is clearly and markedly stronger than in the case of matting agents based on electric arc silica or hydro-thermal process silica. It is impossible to state the secondary particle size in such special types of fumed silica, as their primary particles are agglomerated to form branch chains, as can be seen in Fig. 2.

For this reason the special silica must be thoroughly dispersed. When compared with other matting agents, it has the lowest matting efficiency but the best transparency. Another matting agent is a pure silica obtained by an electric arc process. The materials used are quartz and coke. As high reaction temperatures occur in the electric arc, the resulting silica is very inert. Therefore, both the ignition loss and the absorption of atmospheric moisture are small. It has a compact secondary structure with particles of 2 to 15 microns, composed of small primary particles.

However, with intense dispersion a certain amount of disintegration of the secondary structure can occur, which reduces the matting efficiency and in-creases the thickening effect undesirably. A hydrothermal process silica is produced by a special wet process. Apart from its higher drying and ignition losses, it differs from the electric arc silica, particularly in its secondary particle size, which is in the region of 1-10 microns (Fig. 10).

The secondary particles can also be dispersed under the effect of strong shearing, again resulting in a loss of matting efficiency. Other silica based matting agents may have an organic surface treatment. They are produced by a special wet process and are similar to the hydrothermal process silica with respect to moisture content and matting efficiency. The suspending behaviour of these special silicas, in contrast to other matting agents, is improved by the organic coating. In particularly critical coatings, it may still have a slight

2.8% matting agent, gloss 5.5%
Oblique light, magnification 1:60
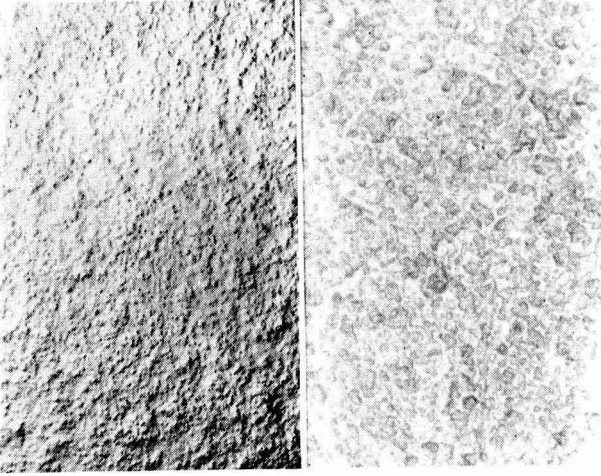
Vertical light, magnification 1:70

Fig. 8. Electric arc silica

4% matting agent, gloss 6.0%
Oblique light, magnification 1:60

Vertical light, magnification 1:70

Fig. 7. Hydrothermal process silica

Gloss 6.5%
Oblique light, magnification 1:60

Vertical light, magnification 1:70

Fig. 6. Fumed silica with particle size 40mm
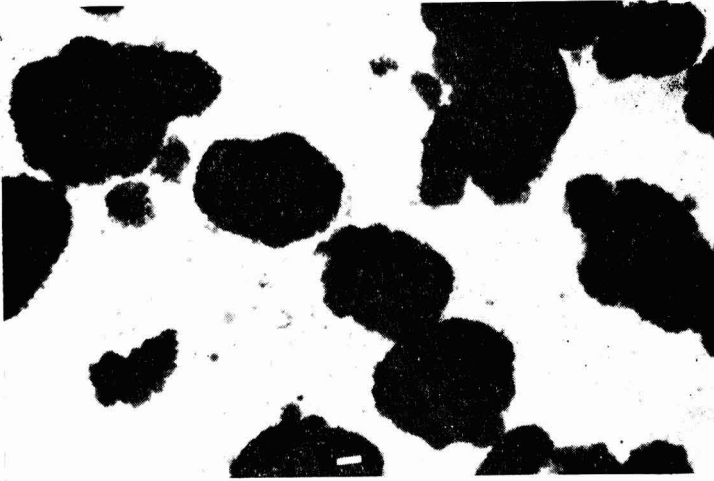
Fig. 9. Electron micrograph of electric arc silica
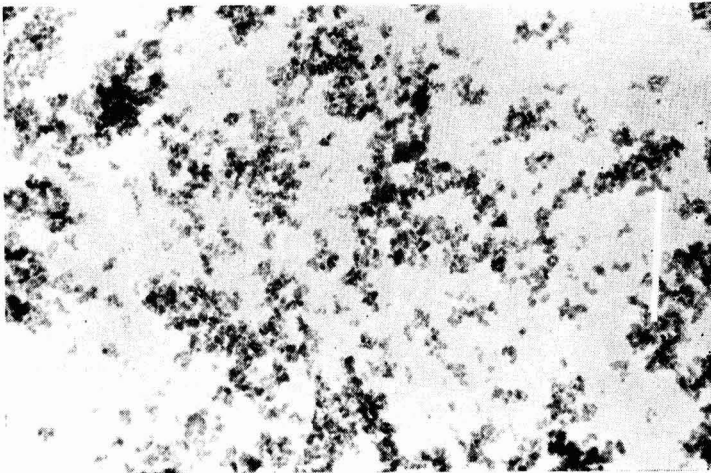
Fig. 10. Electron micrograph of hydrothermal process silica

tendency to settle. However, any separation that may occur is eliminated by slight agitation. The simultaneous use of wetting agents to improve the suspension properties is unnecessary.

Practical usage

From the foregoing data on matting agents, it can be seen that their secondary particle sizes differ, or, as in the case of the matting grade fumed silica, are not determinable. Because of its larger particle size, the electric arc silica exhibits the most marked matting effect with most coating systems. Therefore, it is chiefly recommended for coatings which are difficult to matt because of the composition and percentage of the binder. In this respect, unsaturated polyesters,

one- and two-component polyurethane finishes, air-drying alkyd, and epoxy systems should be noted. For the incorporation of electric arc silicas, hydrothermal process silicas and the organically coated silicas, dispersion with a high speed mixer is desirable. However, in the case of the hydrothermal and organically coated silicas, excessive dispersion should be avoided as far as possible. In the case of the electric arc silica there is a possibility of improving the surface smoothness of the matt film by careful milling.

In contrast with the three preceding matting agents, fumed silica must be milled. Brief milling in a ball mill is recommended. The milling time should not exceed eight hours, however, or the secondary particle size structure of this material is excessively reduced. The matting effect is thus reduced and a marked thixotropy sets in, which in most cases is undesirable in matt or semi-gloss finishes.

Another advantage of the three matting agents described above is the outstanding improvement in mar and buffing resistance, although this is less pronounced in the case of the fumed silica.

Finely divided aluminium silicate

The paint industry uses finely divided aluminium silicates as extenders in emulsion paints.

Table 1. Properties and analysis

BET surface area	m^2/g	110
Average primary particle size	millimicron	30
Bulk density	g/l	150
Tap volume	ml/100g	700
Moisture (2h at 105°C)	%	6
Ignition loss (2h at 1000°C)*	%	7
pH-value (5% aqueous suspension)		10.4
Specific gravity	g/cm^3	2.05
Refractive index		1.46
Whiteness value at 460 mμ	%	98
Brightness reference value A	%	95
SiO_2	%	76
Al_2O_3	%	8.5
Fe_2O_3	%	<0.05
Na_2O	%	7.5
Grit by Mocker	%	<0.01

*of material dried for 2 hours at 105°C

As shown by the data in Table 1, the material concerned is a finely divided substance with a large surface area. It can be seen that the particle size is indicated at 30 mμ. The surface area, measured by the BET method, is 110 m^2/g. Although the primary particle size is approximately 30 mμ the material does in fact have a secondary structure of agglomerated particles.

In Fig. 11 the particle size distribution curve of aluminium silicate is shown. It demonstrates the very narrow particle size range of precipitated aluminium silicate. As compared to natural aluminium silicate, the X-ray structure is
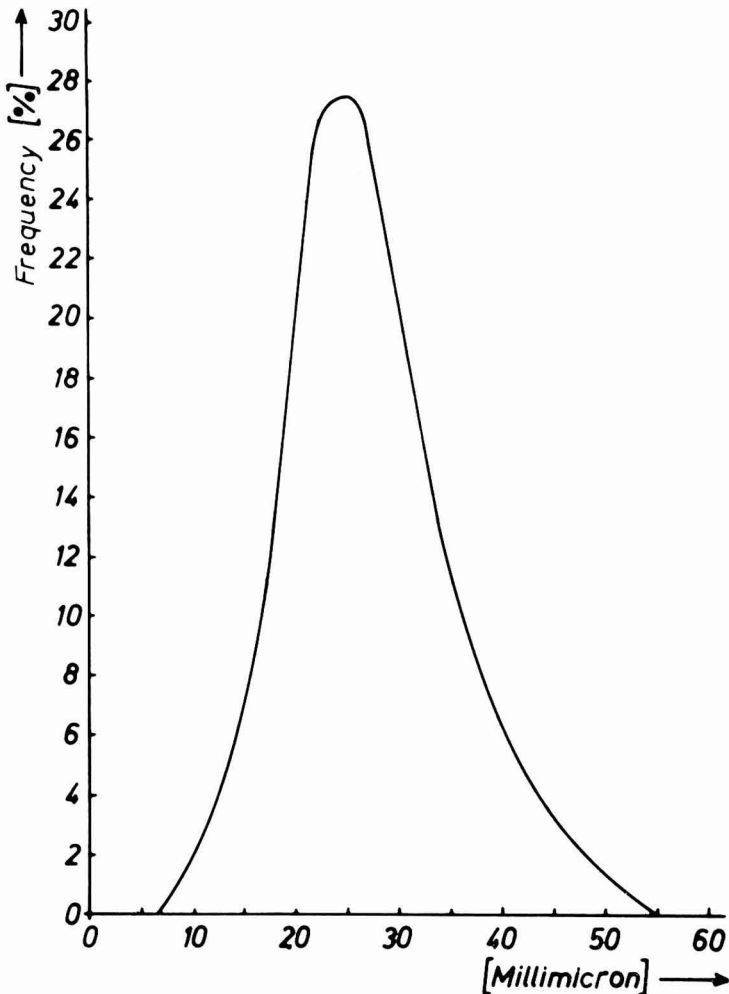
Fig. 11. Particle size distribution of an aluminium silicate

amorphous and, contrary to the crystalline structure of natural silicates, it is also whiter.

The use of aluminium silicate in emulsion paints offers some important advantages, among which is the possibility of replacing 25 to 30 per cent by weight of the white pigment in the paint formulation. Through this substitution the degree of whiteness is increased but not at the expense of hiding power. At the same time, the paint after application becomes more resistant to dry and wet scrubbing, owing to the better packing of the pigment and extenders.

Although the precipitated aluminium silicate has an extremely fine particle size, it still wets readily in water and mixes evenly under the action of an agitator. Therefore, no milling or pre-dispersing is necessary. Like the usual pigments, it can be incorporated into emulsion paints in the customary manner. The
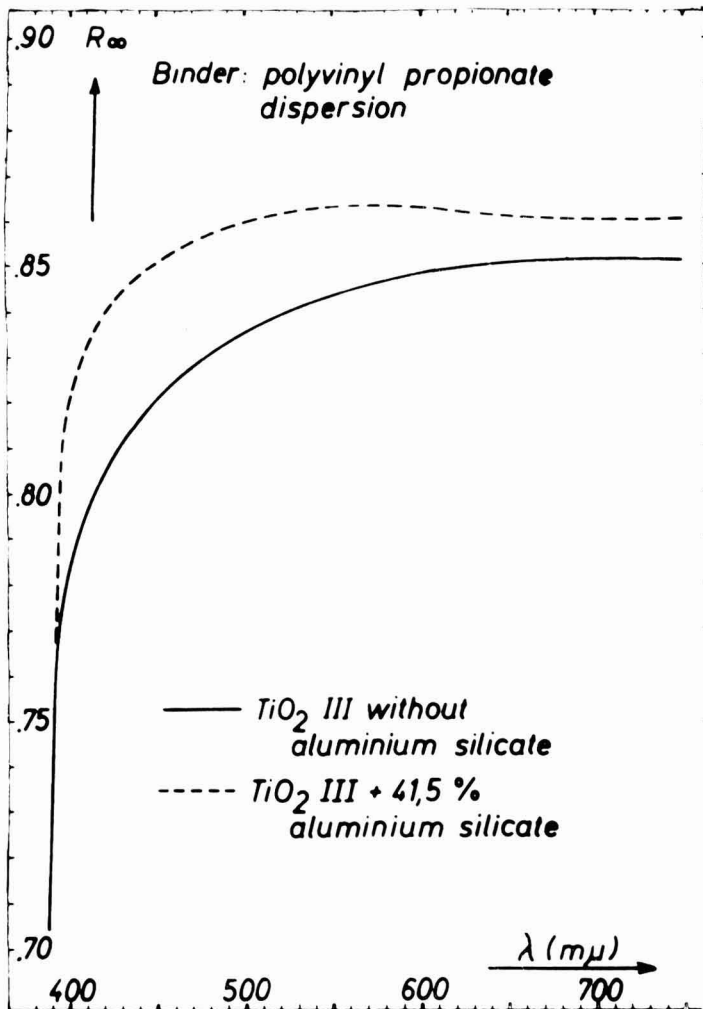
Fig. 12. Performance of precipitated aluminium silicate in conjunction with TiO₂

following diagrams in Figs. 12 and 13 demonstrate the superior performance of precipitated aluminium silicate in conjunction with lithopone and titanium dioxide, using two ordinary commercially available binders.

Measurements by light reflection have shown that the ideal quantity to be incorporated is 5 to 6 per cent of the weight of the complete emulsion paint. To quote an example, if a paint formulation includes 20 per cent of titanium dioxide, a quarter of this can be replaced by precipitated aluminium silicate to give 5 per cent aluminium silicate and 15 per cent titanium dioxide. The incorporation of aluminium silicate also has a beneficial effect on the storage stability, with respect to the viscosity performance of the emulsion paint, whereas the same paint without aluminium silicate tends to increase in viscosity.
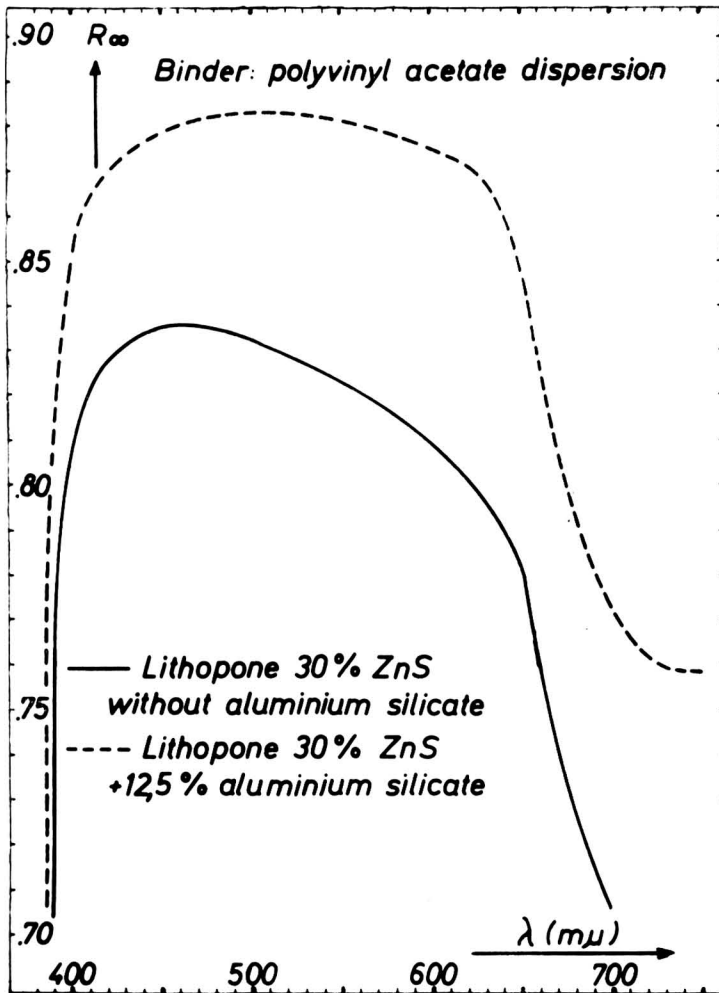
Fig. 13. **Performance of precipitated aluminium silicate in conjunction with lithopone**

The action of the aluminium silicate is due to the fine particles that fill the interstices between the coarser pigment particles, thus keeping them in an optimal distribution and preventing re-agglomeration.

Emulsion paints made with precipitated aluminium silicate have been found to stand up well to various climatic conditions over several years. The only restriction is that the percentage incorporated ought not to exceed the previously mentioned 5 to 6 per cent by weight of the complete paint.

Conclusions

In conclusion, the advantages conferred by the use of precipitated aluminium silicate in emulsion paints can be summarised as follows:

cost saving through the partial substitution of expensive white pigments,

increased efficiency of the white pigments,

less pigment settling due to the finely divided state of the precipitated aluminium silicate,

stable pH and viscosity during storage,

good durability and diminished dirt pick up.

[Received 24 April 1970

Next month's issue

The Honorary Editor has accepted the following papers for publication, and these are expected to appear in the January issue.

Foundation Lecture: "Human relations and communications in industry," *by Sir Paul Chambers*

"The dispersion of carbon blacks in paint and ink systems," *by W. M. Hess and M. D. Garret*

"Design and operating principles of high-speed dispersers," *by F. K. Daniel*

Reviews

"Bitumen und Teerlacke" is published in a plastic cover as Volume 8 of Lacktechnische Schriften, at a price of DM 48,00. The book is offered as having 365 pages, but some 40 of them are advertisements, etc., and placed very obtrusively they are.

The text is meant to appeal both to the paint formulator and the user of tar- and bitumen-based paints, which is a weakness from the former's point of view, because about three quarters of it are to him common knowledge, and a fair portion deals with definitions and the difficult nomenclature of the subject in the German language and with comparisons of American usages.

Literature and patents are generously quoted, and the patents very frequently fully discussed.

The subject index, which appears to be reasonably sized, is however incomplete; to give an example the item "polyamide—amine" is referenced twice, whilst your reviewer found at least four more mentions.

Dr Depke "knows his onions". What he writes is sound and on a scientific basis. The book is for practical use and from our readers point of view interesting as far as they require information regarding combinations of bitumen or tar with synthetic resins—especially the reactive types—of which those chapters dealing with epoxides and polyurethanes are the most useful.

There is very little to criticise. On page 79, hot incorporation of chlorinated synthetic resins is said not to be carried out at temperatures "over 180°". More thorough treatment of the risk of blooming with some bitumen and stearin pitches in straight or combination varnishes would be valuable. The reviewer would not quote, as is done on page 159, an insufficiently checked formulation for a "workable" low zinc dust content paint. On pages 190 and 200, there is a mix-up of suppliers of special pitches, i.e. Union Carbide with United Coke and Chemicals Co. Ltd.

The author has achieved his aim of usefully discussing all the problems connected with his subject from the primitive solution to the complex catalysed combinations.

M. HESS

Large users of organic peroxides may well consider the purchase of this volume justified, purely for its long first chapter by Magelli and Sheppard. This is comprehensive, eminently readable and can only be regarded as an admirable exposition of the commercial and near commercial field, although it is unfortunate that the section devoted to safety could not have been extended or alternatively greater emphasis on hazards be placed throughout the chapter.

United Kingdom users must also remember that we are tending to adopt or even improve on continental safety standards, hence certain common U.S. products referred to in the text are no longer available here. Chapter II, which attempts to present the viewpoint of the main current peroxide users, the polymer chemists, although well written is very abbreviated; perhaps we can look forward to more detail on peroxides for polymerisation processes in later volumes. This current volume should indeed appeal much more to the preparative chemist than to the polymer producer or those undertaking cross-linking operations and curing of thermosets.

The peroxy ester stage is well set by Singer, whilst Sosnovsky's contribution on base-catalysed autoxidations and metal ion catalysed reactions of symmetric peroxides and peroxyesters should stimulate interest and experimentation in these fields. No doubt the trouble-shooting polymer chemist will also learn something of the effect of those radicals which did not become part of the growing polymer chain and the redox systems which failed to achieve the required polymerisation rate. Peracids receive exhaustive and excellent treatment, occupying over 200 pages, and the inclusion of the first half of Chapter 7 despite its apparent overlap with Chapter 6 is well merited. The layout of the preparative details therein could indeed serve as a model for workers in this field.

Prevention of peroxide formation is perhaps a major objective at the Thornton Research Centre, and from there comes comment on the re-arrangement and cyclisation of peroxy radicals leading, it is believed, to "knock" in internal combustion engines. The chapter is essentially concerned with the fate of peroxide intermediates and again should stimulate the preparative chemist, the polymer producer, perhaps, learning something of the fate of those radicals which were not utilised efficiently. The absence of incomprehensible mathematics is particularly applauded and this is also true of the chapter on thermochemistry of peroxides and polar reaction mechanisms.

In all, an interesting volume of very high standard and with a minimum of overlap which, with its two companions yet to appear, must become the standard treatise in this field.

R. CALVERT

SOLID POLYURETHANE ELASTOMERS

By P. WRIGHT and A. P. C. CUMMING. London: Maclaren & Sons, 1969. pp. xxi + 317. Price £6 10s.

This excellent book will serve as a source of reference for all forward thinking paint chemists engaged with the problems of coating these materials.

A brief historical introduction helps to clarify the types of solid polyurethanes, and the second chapter describes the essential chemistry, without too much elaboration. It is to the credit of the authors that this section is as readable as the subsequent chapters on industrial applications.

Manufacture of raw materials, physiological effects and analytical procedures are described and there is an adequate number of references for further reading.

In the sections dealing with cast, millable and thermoplastic polyurethanes, the various materials are described by manufacturer, by trade name, and by the commercial reference number. There is certainly no evidence of any bias towards the products marketed by the authors' company.

Final chapters deal with applications, economics and conclude with an interesting chapter on future developments.

One feature of this book that the reviewer particularly liked was the appendix linking the trade names with the supplier and a brief description of the chemical type.

Author and subject indexes are included, but they are not over elaborate.

The layout and quality of printing is first rate, and this book has already become a standard reference in the reviewer's own library.

S. T. HARRIS

Information Received

The Association was pleased to be represented at a recent presentation made by **British Oxygen Chemicals Limited,** when *Vanweld 323*, a new aqueous based vinyl dispersion, was introduced.

BOC claim that *Vanweld 323* combines an aqueous phase and polymer structure such that the adhesion between pigment and polymer particles, which provides the cohesion of the film when formulating above the critical PVC, will be strengthened. In effect, the pigment and extender particles are said to be "welded" together by the polymer. Thus *Vanweld* can be used to give cost savings by formulating at higher PVCs than are normally possible with emulsion systems. Charts were shown demonstrating that the wet scrub resistance of high PVC paints formulated with *Vanweld 323* was superior to those formulated with other emulsion systems.

Data sheets on *Vanweld 323* are available from BOC.

The surface coatings division of **Synthetic Resins Limited,** the newly formed Unilever company (see *JOCCA* 1970, **53,** 826), has recently issued details of its range of surface coatings resins. Composed of the products of the merged companies Beck Koller Limited, Styrene Co-Polymers Limited and Chas. Lowe and Company (Manchester) Limited, the range is claimed to be the broadest available from a single manufacturer. A list of products follows.

Beckosol & Scopolux—oil modified alkyds; *Scopol & Styresol*—styrenated and vinylated oils and alkyds; *Beckogel*—thixotropic alkyds, *Beckurane*—polyurethanes, *Scopon & Beckadrin*—epoxy esters and epoxy phenolic resins, *Beckamine & Super Beckamine*—amino resins, *Scopacron*—thermosetting acrylic resins, *Lustrasol*—acrylated alkyds, *Scopacryl*—thermoplastic acrylic resins, *Beckacite, Super Beckacite & Crestanol*—maleic and phenolic resins, ester gums and metallic resinates, *Beckphen & Crestin*—phenolic resins solutions, *Beckalide*—polyamide resins, *Beckolin*—low viscosity solventless alkyds.

A new cartridge type filter unit, claimed to be suitable for use with any liquid having a low solids content, has been developed by **Stella-Meta Filters.**

The unit consists of a vessel containing a number of precision wound filter cartridges. Both vessel lining and filter material can be varied according to the application required. The unit is self-contained, inlet and outlet pipes being provided in the base of the vessel, leaving the top cover free so that cartridge replacement is quick and easy. A drain plug is incorporated in the base.

A wide range of sizes is available, from a unit containing 36 cartridges 10 inches long, giving a flow of 3,600 gallons per hour at a 5-micron rating, to a unit holding 432 cartridges 10 inches long, giving a flow of 43,200 g.p.h. at a 5-micron rating.

The *Autex Disperser*, a new powder-wetting device developed by the Mining Research and Development Establishment, is to be manufactured and marketed by **Johnson-Progress Limited,** it has recently been announced.

The disperser, which arose out of the need to wet polyelectrolyte powders reliably in an automatic plant, utilises the high speed laminar flow and powerful centrifugal forces acting in a strong vortex. Initial installations are expected to be for water recovery and potable water treatment plants, but applications in other powder wetting fields are being investigated.

also check
your
protection
with
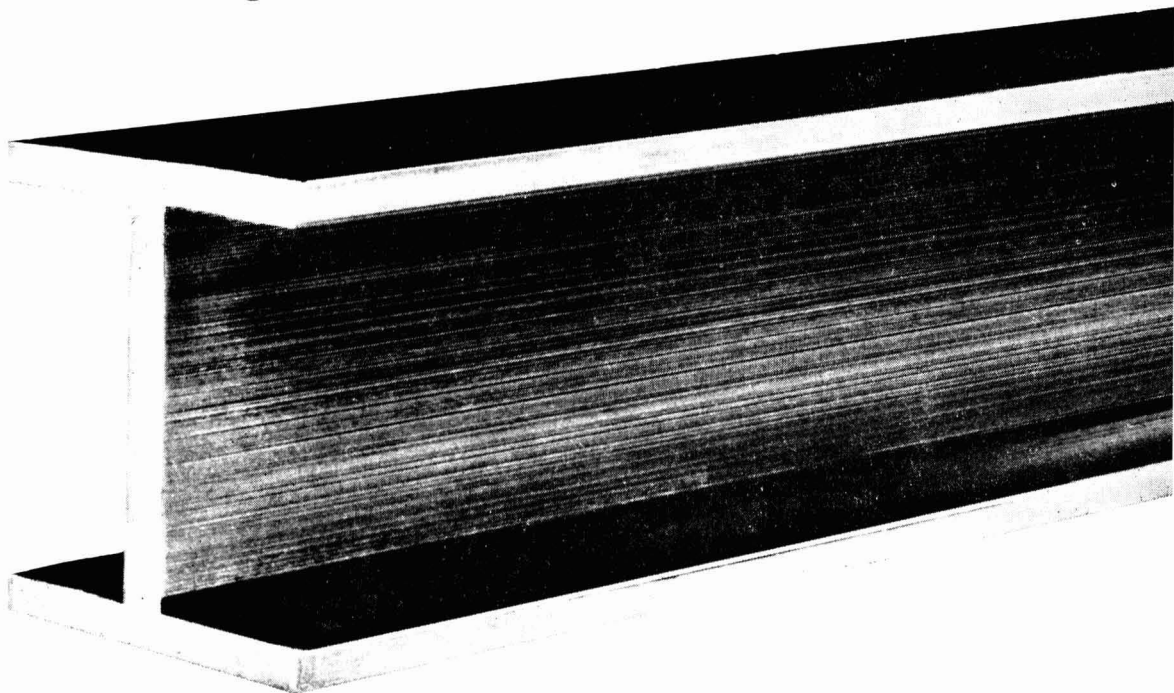
RHOVINAL B

Polyvinyl butyral

a raw material
for use in the manufacture of metal,
wood and paper protective varnishes

RHOVINAL B is particularly suitable
for the preparation of protective groundcoats
for metals of the wash primer type.

An asbestos-based flooring system that is claimed to be Europe's most widely-used is to be marketed in the U.K. by **Kittridge Industrial Flooring Limited.** The rights of the system, named *Fama*, have been assigned exclusively to Kittridge. A jointless, heavy-duty finish is provided by *Fama*, and it is claimed to give a resilient and high durability surface that is sparkproof, fire-resistant, impervious to oil, paraffin, petrol and grease, dust free and has a high grip.

It has recently been announced that agreement has been reached in principle between **Unilever Limited** and **The Metal Box Company Limited** for the sale to Metal Box of **Holpak Limited** and **King Packaging Limited,** the Unilever companies producing vacuum and pressure formings, plastic bottles, injection/blow moulded pots and injection mouldings. The two companies will continue to trade under their own names initially, but will eventually be absorbed into Metal Box's plastics group.

English China Clays Sales Co. Limited has recently issued a product summary, giving brief information on the products being produced for the paint and allied industries. More detailed data sheets on each product are also available.

Agreement in principle for close co-operation between **N.V. Nederlands Staatsmijnen/DSM** and **N.V. Chemische Industrie "Synres"** has recently been announced. DSM has acquired the shares held in Synres by the American company **Allied Chemical Corporation,** amounting to 50 per cent of the capital stock, and has bid for the non-convertible Synres stock quoted on the stock exchange. The co-operation is said to be beneficial to Synres by access to DSM's research facilities and know-how, and to DSM by virtue of the fact that Synres' range of resins for paint and printing inks will provide further diversification of its activities.

NeoCryl B-731-LV is a new thermoplastic acrylic resin from **Polyvinyl Chemie Holland N.V.** Supplied in solution in a low aromatic solvent, the new resin is claimed to offer shorter drying time, better resistance and gloss retention on exterior work and good chemical resistance when combined with long- and medium-oil alkyds.

A new manufacturing process—"sandwich" moulding—which is said to be of major significance to the world plastics industry, has been developed by **I.C.I. Ltd.** The process allows "sandwich" structures, for instance a central core of foamed plastic in a solid plastic outer skin, to be made in a single high speed manufacturing operation. Such sandwiches are superior to conventional plastics in their combination of rigidity and good surface finish, and may well compete with metals in the automobile, electrical, building, packaging and engineering industries. Various combinations of thermoplastics may be used, and the core can be foamed or solid.

Armour Hess Chemicals Limited has recently published a revised version of *Technical Bulletin G27/4,* entitled "Armostats—permanent antistatic agents for plastics". Armour Hess states that the tremendous worldwide interest in antistatic plastics and the rapidly changing technology require that technological literature be constantly brought up-to-date, and for this reason the booklet, originally published in October 1969, has already been revised and reissued.

Hoechst U.K. Limited has recently moved to new offices in Hoechst House, Salisbury Road, Hounslow, Middlesex. The move to the new premises, which are said to represent some of the most modern office accommodation in London at the present time, has been made necessary by the tremendous growth of the company over this year.

"Zinc oxide versus mildew in paints" is the title of a new 12 page booklet published by the **Zinc Development Association,** in co-operation with the **Zinc Pigment Development Association.** Intended as a reference guide to the use of zinc oxide to inhibit fungus growth, the booklet comprises brief notes made from abstracts published in "Zinc Notes" over the past 15 years.

Four new colours have been added to the **Blue Circle Group's** *Sandtex* range of exterior masonry finish. The new colours, *Wedgwood Blue, Mid-stone, Etruscan Red* and *Jonquil,* bring the total *Sandtex* range to 21 shades.

Degussa has recently issued *"Printex 400*—carbon black for typographic and offset inks", a booklet giving technical data and suggested formulations for *Printex 400* in these applications.

A new water-resistant acrylic based thickening agent, *Viscalex HV30,* has been introduced by **Allied Colloids Manufacturing Co. Limited.** The new product, which is supplied in the form of a fluid, easily handled emulsion, is claimed to offer the advantage over other types of thickeners that it dries to give water resistant films. Intended for thickening most water based systems, it is claimed to impart improved wet scrub resistance in low cost, high PVC paints.

The Metal Finishing Division of **The Pyrene Company Limited** has recently issued a new price list for its *Gold Seal* range of steel, aluminium, ferrous and non-ferrous test panels.

It has recently been announced that **Tioxide S.A.,** the French wholly-owned subsidiary of **British Titan Products Company Limited,** is to expand its Calais plant producing *Tioxide* titanium pigments to a capacity of 60,000 metric tons p.a. Work is expected to be complete in mid-1972.

A new company, **Infra-Red (London) Limited,** has been formed to manufacture electric and gas fired infra-red process plant for a wide variety of industries.

A range of standard designs of high intensity emitters has been produced, and descriptive literature is available. The company is also interested in making special purpose process plant for drying, baking, annealing, stoving, etc. to customers' requirements.

The **Building Research Station** will be 50 years old in 1971 and, to celebrate its golden jubilee, open days will be held at Garston between Wednesday 9 June and Wednesday 16 June 1971. At the same time, a golden jubilee congress is to be organised. Other special exhibits, film shows and publications are planned, including a history of the BRS written by Dr F. Lea, a previous BRS director.

Section Proceedings

Hull

Panel Discussion Evening

The first ordinary meeting of the Hull Section was held at the Queens Hotel, George Street, Hull on 5 October, under the chairmanship of Mr F. N. Lythgoe. Short talks were given by members of the Section as follows: Mr F. D. Robinson of Laporte Industries Limited on "Chloride process titanium dioxide"; Mr L. Tasker of Laporte Industries Limited on "The future of synthetic resins"; and Mr P. Adamson of Reckitts Colours Limited on "Recent developments in inorganic pigments".

The speakers were successful in their main purpose of provoking comment and discussion, and no summary of their talks will be attempted here. During the discussion period which followed, questions were asked on a wide variety of topics including: the future growth of plastisols and organosols, the sales potential and development of water-based gloss paints, the relative merits of gloss and semi-gloss paints, flocculation and flotation, and the durability of acicular pigments. Twenty-two members and three visitors were present.

J.A.H.

London

European Liaison Lecture: Rheology and processability of printing inks

The first meeting of the session was held on 14 October 1970 at the Borough Polytechnic with Mr J. E. Pooley in the chair. Mr C. D. Rosted of Sadolin & Holmblad, Copenhagen, gave the European Liaison Lecture under the above title.

Mr Rosted said that many properties of printing ink were not yet measurable, and the experience of the technician was still important in maintaining reproducibility from batch to batch; it was desirable that the properties should be expressed in figures. Rheology was of the greatest importance, and it was one of the first properties to be studied; another property was tack, which was related to picking of the paper surface. The development of the Inkometer in 1936 enabled an operator-independent figure to be obtained, but the Inkometer number was a complex of various physical properties. Viscosity was measured using the Ferranti-Shirley or the Weissenberg cone and plate viscometers, or the Laray instrument. Only a few inks were Newtonian, in most cases the curves for offset or letterpress inks showed plastic flow. At a suitable high shear rate the slope described the plastic viscosity. The intercept was a measure of the shortness of the ink, and the area between the ascending and descending curves was a measure of thixotropy, which was specific to the particular instrumental measurement conditions.

Various equations, e.g. that of Casson, had been proposed to express the behaviour of inks, and Mr Rosted outlined their ranges of application. There was quite a good correlation between thixotropy and shortness, and this was in agreement with experience that a short ink was more likely to hold back in the duct than a long one.

Mr Rosted described some experimental work in which two series of inks had been prepared, in one of which variation in properties had been made by addition of a gel varnish, and in the other by variations in the level of pigmentation. Inks had both viscous and elastic properties. The splitting of inks on the roller took place by cavitation, followed by the formulation of strings; with no elasticity this would not be possible. As the ink passed through the nip there was a perpendicular force tending to force the rollers apart, and the balance between viscous and elastic properties deter-

mined the rate through the rollers. There was some return flow, which contained emulsified damping water and paper dust. Consequently, the ink tended to dry on the rollers.

The effect of plastic viscosity and shortness on ink transfer and screen dot sharpness was studied; these experiments were made on a single colour offset press. Prints were made with the same amount of ink per square centimetre on the two series of inks. The layer thickness was taken as a measure of ink transfer. The maximum was determined for the two series of inks, and identical results were obtained by practical printing and by laboratory tests. The prints were finally used to determine the relation between screen dot sharpness and rheological properties.

The lecture was followed by an extensive discussion, after which a vote of thanks to the lecturer was proposed by Mr J. A. L. Hawkey.

V.T.C.

Southern Branch

Driers

The first meeting of this session was held at the Pendragon Hotel, Southsea, on 13 October 1970 when Mr J. Turner, of Hardman & Holden Ltd., presented his paper entitled "Driers", with special reference to the possible impact of co-ordination driers on paint and printing ink formulations.

Only 17 members and guests were present; no doubt more would have attended if they had realised that an "old hat" subject would be completely transformed in the hands of Mr Turner. Those who attended were treated to a host of new ideas which stimulated a long and lively discussion period after the end of the lecture. The interest was so great that the chairman, Mr B. A. Richardson, had to perform the unusual task of asking for a final question so that visitors could catch the last train to London.

In his lecture, Mr Turner briefly considered the conventional driers so that they could be compared with co-ordination driers, his main topic. Co-ordination driers were at present based on two metals, aluminium and zirconium, but it might be possible to produce similar products based on chromium and titanium. The main principles were explained; polymerisation was carried out using electron donating groups, for example -OH and -COOH, within the resin, in complete contrast to the oxidation of unsaturated bonds within the resin in conventional drying systems. With these compounds it was possible to produce a surface coating which dried by the formation of a gel structure in a matter of seconds. This would have obvious advantages in speeding up the process of painting components since these could be stacked immediately after dipping.

The overall theme of Mr Turner's lecture was to stimulate ideas about entirely new paint systems, since there was an attitude which often prevailed in the coatings industry, of adding yet another component to cure a defect in a product. Paint formulations were unnecessarily complex at present but with co-ordination drying paint technologists could develop entirely new types of coating composition.

It is hoped that the full text of Mr Turner's paper will appear in a later issue of the Journal.

T.R.G.C.

Manchester

Industrial espionage

The inaugural meeting of the session was held at the Manchester Literary and Philosophical Society on 9 October, under the chairmanship of Dr F. M. Smith. The Lecturer was Mr R. B. Matthews, of Management Investigations Limited, and his subject was "Industrial espionage".

Mr Matthews disclaimed any participation in industrial espionage, he merely organized defence against it. With a personal background of military intelligence he had thought his experience would be valuable in commerce but had found no organization to join. He prepared himself by contacting industrial spies over a period to glean their methods and then set up a counter intelligence organization.

He asked the audience to forget the images projected by T.V. and films, where electronic gadgets always worked perfectly; in practice this was far from the case. He listed four groups of industrial spies, first, the opportunist with accidental access to material which he tried to sell to a competitor—these were amateurs and easily caught. Industrial espionage was not a criminal offence, but theft—for example of company paper—was.

Secondly, there were ferrets who collected general information for sale to the press unless a more valuable customer appeared, perhaps a professional agency.

Thirdly, the professional team, comprising a technician, often an ex political spy, a man with knowledge of the industry, a marketing man, and the man who put up the capital. The lecturer expressed high regard for the efficiency of this team.

So far none of these groups was operating directly under commission from an industrial firm. The fourth type, comparatively new to the UK, was growing fast and would cause great damage over the next 10 years. They were directly sponsored by an industrial company, had a highly specific objective, information and contacts from the sponsor.

Mr Matthews's presentation was lavishly illustrated by examples and anecdotes, both being confidentially anonymous. He stressed that he would not guarantee 100 per cent total security and pointed out that the degree of security exercised must be related to the cost of the operation and the value of the property being protected.

He concluded with a selection of slides illustrating electronic aids "recovered" following investigation. These ranged from boxes the size of a transistor radio to gadgets less than the size of a threepenny piece, comprising microphone, transmitter, power source and aerial and capable of transmitting over a distance of 100 feet!

After a discussion in which no question went unanswered but full professional confidentiality was preserved, the vote of thanks was proposed by Mr F. Redman and carried with acclamation by the 80 members and guests present.

D.A.P.

Midlands

Wood protection

The first meeting of the Midlands Section for the session 1970-71 was held on Friday 25 September, at the Chamber of Commerce, Birmingham, 19 members and 8 guests being present, with Mr H. J. Griffiths, the Section Chairman, presiding. A lecture on "Wood protection" with particular emphasis on exterior joinery, was given by Mr G. L. Holbrow of the Paint Research Station, with the assistance of his colleague Mr A. F. Sherwood.

Mr Holbrow began by showing slides demonstrating some of the worst types of paint failure on weathered exterior joinery, the photographs being taken of window and door frames in the building of the P.R.S. but typical of the failures seen in any building in the land. The work described had been going on for a number of years at the P.R.S., testing commercial and development paints on a variety of timbers. In the last year these studies had gained new impetus owing to the placing of a research contract by the Ministry of Public Buildings and Works. Initial results in this new programme were discussed; very real progress was expected with the project over the next two years.

Some measure of the importance of this work was that the cost of painting wood in the U.K. is estimated at £100 million per annum, by far the largest proportion of which was in labour costs. Therefore, any effective increase in the durability of painted exterior joinery should save the nation a great deal of money. The simple objective of the present programme was to develop a complete system of preservative, primer, undercoat and finish which would effectively increase durability and reduce maintenance costs.

Mr Holbrow and his colleagues were well aware of the difficulty of the task and in particular of the need to consider the contributions made by all components of a test piece to its success or failure. Not least of these was the wood itself, whose variability, even along the length of a given plank, was wide enough to confound an ill-prepared experimental sequence. The sequence of steps taken to ensure valid results by extremely careful selection of timber for each programme was described. Selection was made not only of high quality timber but also to cover each range of source, structure and porosity, each sample being carefully mapped before painting. The general aim was to develop a system suitable for protecting comparatively low quality timber and tolerant of malpractice in paint application and subsequent handling.

The failures illustrated by the slides were the result of excessive water entering the wood, leading to paint failure and accelerated water entry. Controlling factors in the process were the porosity of the wood, the permeability of the paint film and the presence of faults in the protective film such as mechanical damage, unpainted areas or the wicking effect of raised fibres. Wood was hygroscopic and readily took up water which was absorbed onto the cell walls by hydrogen bonding to the cellulose units. For general soft woods, saturation by this process was achieved at approximately 30 per cent water content, as evidenced by swelling reaching a maximum. Beyond this point, water began to fill the capillaries and a water-logged state was obtained. Fungal spores were always present, and when the water content reached 20-25 per cent, fungal growth might have already set in. Such timber was described as ponded sapwood and is very highly porous, soaking up excessive amounts of preservative. Some 3-5 per cent of the Scots Pine used in joinery work is in this state.

Mr Holbrow discussed some of the factors in the entry of water into wood; for instance water vapour penetrated end grain at ten times the rate of penetration on the face and liquid water penetrated at one thousand times the rate of water vapour. The P.R.S. team used sorting tests for wood samples, including rate of absorption of isopropanol and pressure loss from a pressurised head in contact with the surface via a rubber ring.

The basic descriptions of systems so far tested were given. Preservative solutions were discussed, of which the active ingredients were a fungicide to prevent rot when local high water contents temporarily arose in the wood, and a resinous binder to seal the wood and reduce water take up. Permeability measurements were reported on a number of free paint films using a Payne cup. A significant result was that, in contrast to emulsions, alkyds gave films of low water liquid permeability, approximately equal to that of the water vapour. Permeabilities increased with both relative humidity differential and increase in temperature. Problems usually occurred at the cold exterior face of joinery, where the water content of the wood was usually high and paint permeability low.

The present experimental sequence at the P.R.S. comprised:

initial sorting of paint system for basic drying and adhesion performance;
6 months' outdoor exposure on panels shaped to give a water trap;
Exposure in a specially developed wet/dry cycle apparatus

24 hour cycle 2 hours' water spray to give   100 per cent RH
                       5 hours in 20 per cent RH air stream to reduce to   60 per cent RH
                       17 hours with humidifier to hold   60 per cent RH

panels weighed before and after water spray and the fluctuations in water content recorded;

selected systems exposed in a box composed of miniature window frames.

The paper was well received and provoked an interesting discussion when the Chairman threw the meeting open to questions. The Hon. Social Secretary, Mr A. S. Gay, proposed a vote of thanks.

R.J.K.

Trent Valley Branch
Metrication and paint packaging in the future
The first meeting of the new session of the Trent Valley Branch of the Midlands Section was held on Thursday 1 October at the British Rail School of Transport, Derby, under the Chairmanship of Mr E. Hare.

Before an audience of 19 members and guests, Mr R. B. Beazley, of the Metal Box Co. Ltd., gave a broad outline of metrication in the paint industry with particular reference to European standards, rationalisation of can sizes, etc.

Already approximately 85 per cent of the world's population was using the metric system, the main "outsiders" at present being the U.K. and America.

In deliberating on the overall question of new pack sizes it had finally been decided to adopt the following range for round lever lid paint tins:

CAPACITY
100ml
250ml
500ml
1 litre
2.5 litres
5 litres

Proposals for the metric oblong range of containers was:

CAPACITY
125ml
250ml
500ml
1 litre
2.5 litres
5 litres

This did, in fact, correspond to the agreed European range. Previously, paint on the Continent had, generally speaking, been sold in numerous weight permutations, but all agreed that standard pack sizes should be universally adopted. The 2.5 litre size container was particularly popular on the Continent, and it was generally thought that the future trend in this country would also move towards the purchasing of larger packs, both in the retail and trade markets. There was a very strong indication over the past years that this would take place, and would doubtless be more apparent when the metric range of packs were regularly in use.

The Paintmakers Association had issued a leaflet giving some information on the topic of metrication, and also endeavouring to give an indication of the likely storage space required for metric packs.

The Metal Box Co. Ltd. had also issued a pamphlet to paint makers detailing the proposed new can sizes, capacities, etc.

In addition, the Paintmakers Association were issuing sample metric cans to illustrate the main differences between imperial and metric sizes.

It could be seen, therefore, that everything was being done at this relatively early stage to assist paint manufacturers to acquaint themselves with the needs of the future.

Mr Beazley then went on to outline the obvious problems that Metal Box, as container manufacturers, would be confronted with when the change-over officially took place next year. At present, they ran two production lines in their factories, one being semi-automatic, where non-standard size cans were made (a somewhat costly process), and the other completely automatic. Little or no manual work was required in the latter, and production ran at roughly 300 cans per minute.

When conversion took place, however, a loss in production was going to be inevitable. Automatic lines would require re-tooling, and the running-in process would also cause a drop in production, for a while at any rate. Mr Beazley explained, therefore, that plans were being made to install "back-up" lines in each of their factories to assist in the change-over period, and it was hoped that this would help to eliminate some of the initial production problems. The intention was to review can stocks with customers six months before metrication, after which it was hoped a smooth change-over would be feasible, i.e. imperial size cans one day, metric the next.

Can manufacturers had numerous problems of their own to overcome in connection with production, bulk packaging and transportation of the new containers, but great headway had already been made on most of these.

Finally, Mr Beazley spent a short period describing some of the work being carried out by Metal Box's design centre on new types of paint containers, with the retail market very much in mind. Market research in this field was extensive and already numerous trials had been carried out with, for example, production of paint cans with easily removable ring-pull lids.

The cost of production of paint cans was still relatively low compared with other types of metal containers, but it was hoped that paint manufacturers would be prepared to pay more in future for more sophisticated containers, which would obviously have a greater attraction for the consumer market.

Mr Beazley's talk was well illustrated by a series of slides, and the lecture period itself interspersed with relevant questions (at Mr Beazley's suggestion) with a concentrated question period as a finale.

A vote of thanks was proposed by Mr D. J. Holmes for this most interesting and enlightening talk.

D.F.G.

Foundation Lecture
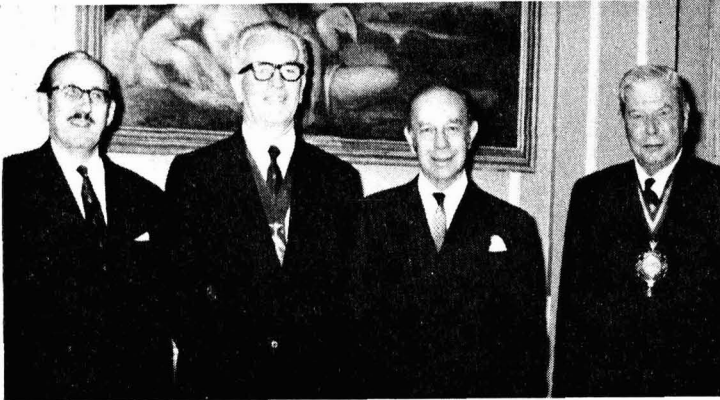
Seen before the lecture (left to right) Mr R. H. Hamblin (Director & Secretary) the President (Mr A. S. Fraser) Sir Paul Chambers, and Mr H. A. Collinson (Master, Painter-Stainers)

Human relationships and communications in industry

On Thursday 8 October, nearly 100 Members gathered in the Court Room of the Painter-Stainers' Hall, Little Trinity Lane, London, to hear Sir Paul Chambers, KBE, CB, CIE, deliver the Foundation Lecture. Sir Paul, ex-Chairman of ICI Ltd., Past-President of the Institute of Directors, President of the Advertising Association and Chairman of the Royal Insurance Co. Ltd., spoke on "Human relationships and communications in industry". The lecture, reflecting Sir Paul's wealth of knowledge on the subject, was very well received. The Association is pleased to have obtained the paper for publication in the January 1971 issue of the *Journal* and, in view of this, no attempt will be made to report the lecture here.

After the lecture, Mr R. P. L. Britton, the only one of the three surviving Founder Members of the Association able to attend, gave a vote of thanks to Sir Paul. He said he was sure that anyone who read the newspapers was appalled by the current state of industrial relations, often culminating in strikes

and the other difficulties which seemed to accumulate and never end. He felt sure that if someone as knowledgeable in the field of industrial relations as Sir Paul Chambers were to investigate these matters, improvements would quickly be noticed.

All the audience would equally be aware of the difficulty of human relations, and of how easy it was for misunderstandings to occur. If everybody followed the rules laid down so adequately by Sir Paul, he was sure that they would be much better employers.

A short informal reception followed the lecture, and then the company adjourned to the Dining Hall for the Dinner.

After Dinner, the President, Mr A. S. Fraser, welcomed Members, recalling that this was the fifth Foundation Lecture, and that all five lectures had been held in the Painter-Stainers' Hall. The Association was very pleased to further its liaison with this ancient livery company, and was honoured by the presence of its Master, Mr H. A. Collinson, OBE. He thanked Mr Collinson on behalf of the Association
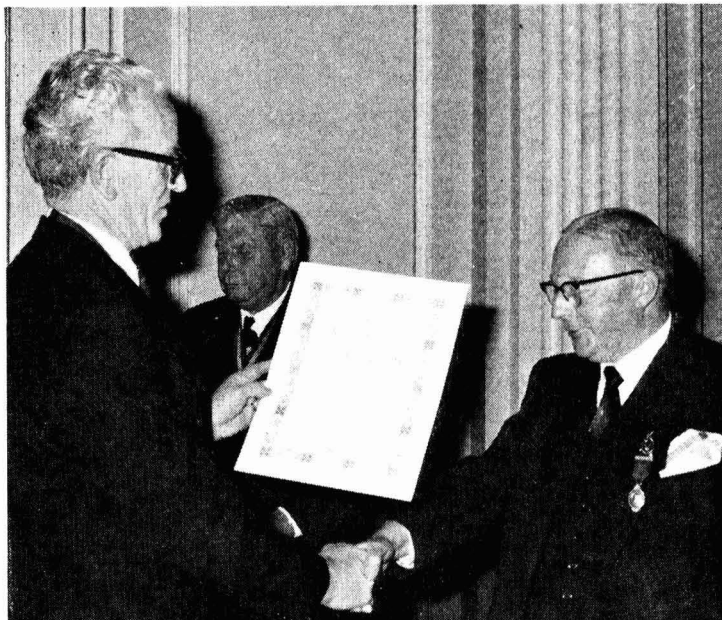
**Dr H. A. Hampton (right) receiving his scroll of Honorary Membership
from the President**

for the use of the Hall on these occasions, and looked forward to the continuation of the liaison through the years to come.

Mr Fraser went on to thank Sir Paul Chambers and congratulate him on his lecture; the Association was honoured that he had given it so much of his time, and appreciated his kindness in so doing.

In recent years, the Foundation Lecture had been combined with the annual dinner at which Council entertained Past Presidents, Honorary Members, Past Honorary Officers, and Founder Members, and there were one Founder Member, seven Past Presidents, three of whom were also Honorary Members, and five Past Honorary Officers present.

Members would have noticed from the report of the Annual General Meeting that Council had conferred Honorary Membership of the Association on two Past Presidents. Unfortunately, neither had been able to be present at the AGM, Dr H. A. Hampton on the advice of his doctor, and Mr F. Sowerbutts

owing to the fact that his wife had just undergone a serious operation—from which, he was glad to say, she had now completely recovered. Both Members were present and Mr Fraser had pleasure in presenting to them their Scrolls of Honorary Membership.

Normally, it had been the privilege of the President at Past Presidents' Dinners to give a report on the state of the Association. However, he was sure that all those present had read both the *Journal* and the Annual Report, and were thus aware of the activities at both Association and Section levels. One of the most encouraging features of the year had been the successful Symposia organised by several Sections, not least that to which he was attached, the Scottish Section, whose Symposium had been combined with the AGM of the Association.

The Association was in good heart, was already embarking vigorously on its second fifty years and was looking
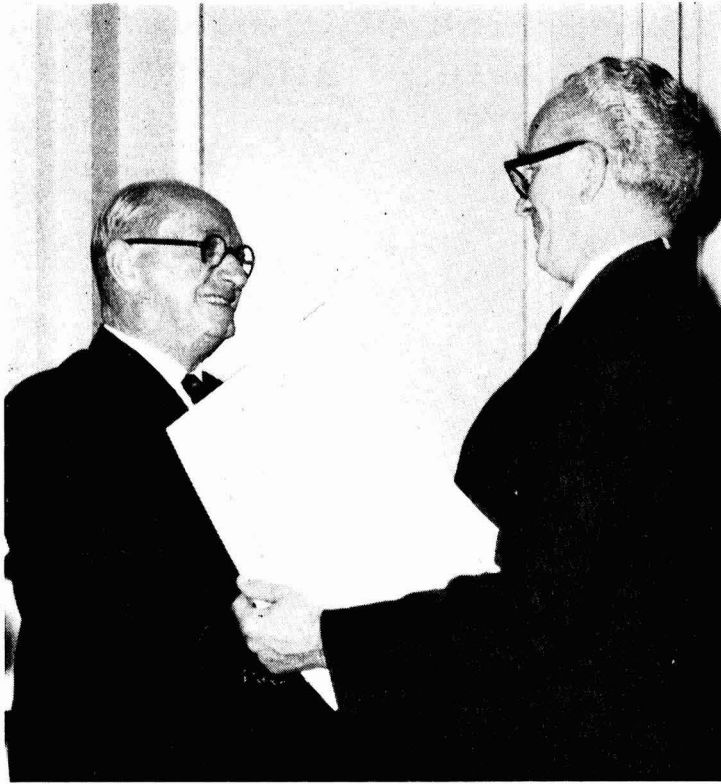
Mr F. Sowerbutts (left) receiving his scroll of Honorary Membership from the President

forward to even greater things in the future. Mr Fraser called on all Members, other than the Founder Member and the Past Presidents, to join in a toast to the Founder Member, the Past Presidents, the Master of the Worshipful Company of Painter-Stainers and the Foundation Lecturer.

In reply, the Master of the Worshipful Company of Painter-Stainers, Mr H. A. Collinson, OBE, thanked the Association on behalf of the guests for the welcome they had been given. He was very appreciative that OCCA used the Painter-Stainers' Hall for its Foundation Lectures, and realised that many of the products with which Members were concerned would be used by the various industries represented in the livery company. He had been very pleased earlier this year to accept the Association's invitation to its Technical Exhibition, where he had been intrigued to find so much detail given to the manufacture of colours.

Mr Collinson went on to say how much he had enjoyed the Foundation Lecture, and referred to the work done by Sir Paul in improving company relations, particularly by his emphasis on the importance of company magazines.

Finally he conveyed the good wishes of the Painter-Stainers to the Association, and thanked the Association, and its Director & Secretary, Mr R. H. Hamblin, for a very enjoyable evening.

R.W.

Sixth Congress of the Federation of Scandinavian Paint and Varnish Technologists

The Presidents of the four associations, (l.-r.) Mr A. S. Fraser (President, OCCA), Mr W. W. Vasterling (President, FSPT), Dr P. Castan (President, FATIPEC), Dr K. Christensen (President, SLF).

The President, Mr A. S. Fraser, represented the Association at the Sixth Congress of the Federation of Scandinavian Paint and Varnish Technologists, which took place in Copenhagen from 7 to 9 September 1970, and conveyed the greetings of OCCA to the congress. It is very pleasing to know that the Presidents of the Association's three sister societies were also present on this occasion; a photograph of the four Presidents, Mr Fraser, Dr K. Christensen (SLF), Dr P. Castan (FATIPEC), and Mr W. W. Vasterling (Federation of Societies for Paint Technology), is shown above.

On the evening of Sunday 6 September, Mr Fraser attended an informal dinner given by Dr Christensen in the Langelinie Pavilion of the Royal Danish Yacht Club.

The congress proper began on Monday 7 September, when the Danish Minister of Commerce, Mr K. Thomsen, delivered the Opening Address, and this was followed by the first of the technical papers. A feature of the congress was the availability of simultaneous translation into English of all papers.

On the Monday afternoon 350 people heard the official OCCA paper, read by Mr L. A. Tysall and entitled "Compositional changes of solvent mixtures during the film forming process," which was well received. On the Monday evening, a banquet was given to mark the 20th anniversary of the Danish Association, and of particular interest to Members of OCCA was the presentation of Honorary Membership of the Danish Association to Mr H. K. Raaschou Nielsen, a member of OCCA, who is Director of the Danish paint research establishment. The SLF president-elect, Mr A. Brantsaeter, was introduced at this banquet; he will take office as president in 1971.

On Tuesday 8 September, technical papers were presented throughout the day, and in the evening a reception took place at the Town Hall of Copenhagen, when the participants of the congress were welcomed by a member of the Town

Council. The reception was followed by an informal visit to the Tivoli Gardens.

The final day of the Congress was devoted to visits to local factories manufacturing paint and allied raw materials, to the Danish Atomic Energy Commission, and to the Danish Paint and Printing Ink Research Institute. The fine support which had been a feature of the technical sessions was continued for these visits.

A full programme was also arranged for ladies accompanying congress delegates, and this included a visit to Elsinore and a visit to the Royal Copenhagen Porcelain Factory.   A.S.F.

Dr H. K. Raaschou Nielsen (right) receiving the award of honorary membership of the SLF from Mr K. Kilsgaard, the President of the Danish Association. The lady in the photograph is Mrs E. Brantsaeter, the wife of the new SLF President-Elect.

Association Conference 4-8 May 1971

Surface properties and appearance

The programme for the Association's 1971 Conference, to be held at the Palace Hotel, Torquay from 4-8 May, was published in the November issue of the *Journal*, and biographies of the authors and summaries of the papers appeared in October and November. Reprints of the biographies and summaries have been prepared, and are available on request.

It will be seen that, of the three days of the Conference, five half-days are taken up with technical activities. On the remaining half-day, the Friday afternoon, the Association's Annual General Meeting will take place. A full social programme for the ladies has also been arranged.

The Council has fixed the registration fees for this, perhaps the fullest conference to date, at £15 for Members, £7.10.0 for wives and £25 for non-members. The Council has again made a concession to Student and Retired Members in fixing a reduced fee of £7.10.0.

The Chemical and Allied Products Industry Training Board will consider the payment of grant, for firms within scope, for attendance at the Conference. Payment is subject to the content of the Conference being relevant to the needs of the sponsoring company and also to the development of the individual attending.

Brochures giving programme and accommodation details, and containing a registration form, are now being circulated, and further copies are available on request.

The closing date for receipt of registration forms is 1 March 1971.

Report of Meeting of Council

A meeting of the Council was held on Thursday 8 October 1970 at Wax Chandlers' Hall, Gresham Street, London, under the chairmanship of the President (Mr A. S. Fraser). There were present 29 members. A welcome was extended to Mr S. Duckworth, who was attending his first Council Meeting as representative of the Manchester Section. Council was pleased to learn that Mr A. G. Holt (Elective Member) had left hospital after an operation and was making satisfactory progress.

Council was informed that for health reasons Miss D. L. Tilleard was unable to continue as the representative of the Association on various committees of the British Standards Institution. Thanks were expressed to Miss Tilleard for her past service and it was agreed to seek the assistance of other members to represent the Association in this way.

It was reported that during the summer discussions had taken place at the Associations offices with the following overseas visitors: Mr L. A. Hill, Hon. Editor of the Oil & Colour Chemists' Association Australia's "Proceedings & News": Mr K. M. Engelbert, Hon. Treasurer of the South African Section and a former Vice-President: Mr P. B. Hunt, the first overseas recipient of the Commendation Award, Past Chairman of the Auckland Section and a former Vice-President: Mr W. W. Vasterling, President of the Federation of Societies for Paint Technology, USA.

The President gave a report on the Conference he had attended in Copenhagen 7-9 September organised by the Federation of Scandinavian Paint & Varnish Technologists. A full report by the President appears elsewhere in this issue of the *Journal*.

Council was informed that arrangements were well in hand for the Associations' Biennial Conference to be held at Torquay from 4-8 May 1971. Brochures would be despatched to all members at the beginning of December for return by 1 March 1971. The registration fees for the Conferences, as recommended by the Finance Committee, were agreed at Members £15, Non-Members £25, Wives, Student Members and Retired Members £7.10.0. Members attached to the Bristol Section only would be able to register at a sessional rate of £3 per session. The Chemical and Allied Products Industries Training Board had recognised the Conference for the purpose of grant to companies in relevant cases. It was agreed that three distinguished technologists from overseas be invited to act as Chairmen at three of the Technical Sessions with the Hon. Research and Development Officer chairing the fourth. Topics for subjects for Workshop Sessions were also discussed.

The Hon. Treasurer (Mr F. Cooper) reminded Council that copies of the half-year accounts had been circulated to members before the meeting and these were accepted, together with the Dinner Dance accounts and estimates for the second half of the year.

The Finance Committee had also considered at its meeting in September the rate charged to non-members for the *Journal* and had decided that, in view of the constant increases in the costs of both printing and paper, and the fact that the price had not been raised since 1965, the annual subscription for the *Journal* to non-members should be increased with effect from 1 March 1971 from £7.10.0 to £10, with single copies charged at £1 each.

Details were given to Council on the number of members removed from the General Overseas and UK Sections for non-payment of their 1970 subscriptions.

The Hon. Editor (Mr S. R. Finn) reported that he had a number of papers in hand for the *Journal* but that he was still anxious to receive as many papers as possible from Section technical meetings this session. The manuscript for Volume VII of the Paint Technology Manuals, "Works Practice", had been sent to the publishers, Chapman & Hall Ltd.

It was reported that Mr A. G. North had agreed to give a paper on behalf of

the Association at the forthcoming Annual Meeting of the Federation of Societies for Paint Technology to be held in Boston from 28-31 October and that Dr W. Carr would also be giving a paper at the same Meeting, for which he would receive a Roon Award.

The Hon. Research & Development Officer (Mr A. R. H. Tawn) gave a short report on his recent visit to the USA during which he had lectured to the Pittsburgh and Houston Societies of the Federation for Paint Technology and at The Paint Research Institute's Annual Meeting in Colombus. On all these occasions Mr Tawn conveyed to the respective organisations the greetings of OCCA, for which Council thanked him.

As Mr Worsdall's term of office as one of the Association's representatives on the Technical Training Board for the Printing Ink and Roller Making Industry would terminate on 31 December 1970, Council agreed to extend an invitation to another member to serve in 1971 with Mr R. M. W. W. Wilson who is the other Association representative.

Council were informed that a Sub-Committee of the Working Party on Forward Thinking (composed of Mr D. A. Bayliss, London Section; Mr M. P. Ford, Bristol Section; Mr D. Morris, West Riding Section and Mr F. D. Robinson, Hull Section) were to meet on 19 October to discuss the best method of preparing a comprehensive report and analysis of the summaries of replies to the Sections' surveys.

On the subject of Education, Training and Qualifications, the special Working Party was given new terms of reference to prepare a scheme in full detail for the introduction of a professional grade for the consideration of Council.

Section reports were given to members by Section Chairmen and representatives and Council was interested to hear that Mr R. Adam, Past Chairman of the Irish Section, was leaving shortly to take up an appointment in Australia and conveyed its best wishes to him in his new post.

It was decided that the date of the next Council Meeting would be Thursday 28 January 1971.

Midlands Section

The top table party; (left to right) Mr W. W. Vasterling (President, FSPT) and Mrs Vasterling, Mr H. J. Griffiths (Chairman, Midlands Section) and Mrs Griffiths, Mrs Penrice and Mr D. Penrice (Chairman, Birmingham Paint and Lacquer Club)

Ladies' Night

The Midlands Section Ladies' Night has now become established as the first Section Dinner Dance of the session and this year was held on Friday 18

September at the Westbourne Suite, Botanical Gardens, Edgbaston, Birmingham. Since the function last year was in the nature of a special occasion to mark the twenty-first anniversary of the

Section, it was not expected that the attendance would be as great this year, and therefore the Committee is pleased to report that as many members and friends were present on this occasion as for the twenty-first anniversary held in September 1969.

This occasion was historic on its own account, since, for the first time, the Section entertained not only the President of the Birmingham Paint, Varnish & Lacquer Club, Mr D. Penrice and Mrs Penrice, but also the President of the Federation of Societies for Paint Technology, to which the Birmingham Club is attached, Mr W. W. Vasterling. Mr and Mrs Vasterling had paid a visit to the UK on their way back from the Conference in Copenhagen organised by the Scandinavian Federation of Paint & Varnish Technologists, a report of which appears in this *Journal*.

The guests were received by Mr H. J. Griffiths, Chairman of the Midlands Section, and Mrs Griffiths, and after Dinner Mr Griffiths welcomed the guests who, as well as Mr & Mrs Vasterling and Mr & Mrs Penrice, included Mr Staples, Chairman of the Midlands Section of the Paintmakers Association, and Mrs Staples, Dr F. M. Smith (Chairman of the Manchester Section) and Mrs Smith, Mr D. H. Tate (Chairman of the Newcastle Section) and Mrs Tate and Mr R. H. Hamblin (Director & Secretary). The response on behalf of the guests, by Dave Penrice, was both witty and amusing and afterwards Mrs Griffiths charmingly thanked the Section for the ladies' gift, which on this occasion was a small portable battery-operated fan.

Dancing continued to the Hiltones and congratulations on the success of the evening are due, once again, to Mr A. S. Gay, Social Secretary of the Section, for the arrangements that he made. A.E.C.

News of Members

At the recent AGM of the Institution of Corrosion Technology, five Members of OCCA were elected as office bearers.

Dr J. Bowler-Reed, an Ordinary Member attached to the London Section, became immediate past chairman.

Mr D. S. Newton, an Ordinary Member attached to the Bristol Section, and Association Hon. Secretary, was elected hon. publicity officer.

Mr D. A. Bayliss and Mr T. R. Bullett, both Ordinary Members attached to the London Section, and Mr F. G. Dunkley, an Ordinary Member attached to the Midlands Section, were all elected to the council of the ICorrT.

Mr J. B. Eckersley, an Ordinary Member attached to the London Section, has been appointed U.S. sales manager for British Titan Products Company Limited.

Mr I. C. R. Bews, an Ordinary Member attached to the London Section, and a past Hon. Editor and Hon. Secretary of the Association, will take Mr Eckersley's place as B.T.P's home sales manager.

Mr E. P. Ashby, an Associate Member attached to the Manchester Section, and previously a technical representative in B.T.P's Manchester sales office, is to join Mr Eckersley in the U.S.A. in December.

Mr T. M. Wright, an Ordinary Member attached to the Midlands Section, has moved from the company's Birmingham office to the Manchester office as technical representative.

Mr W. G. Wade, an Ordinary Member attached to the Bristol Section, has retired from his position as export and home sales director of Golden Valley Colours Ltd.

Congratulations are extended to Mr K. M. Engelbert, an Ordinary Member, Hon. Treasurer of the South African Section, a Past Chairman of that Section and a Past Vice-President of the Association, on being granted an International Rowing Umpire's Licence. Mr Engelbert is President of the South African Amateur Rowing Union and was examined for the licence during the 1970 World Championships in Canada. He is the only current holder of the licence in

South Africa and only the second South African to qualify for the Licence.

City and Guilds of London Institute

Congratulations are extended to the following Members who were successful in the recent City and Guilds examinations in ink technology. The Member's grade and Section are shown in italics.

Subject 250—Printing Ink Technician's Certificate. Part I.

Mr P. D. M. Roberts (*Ordinary— London*)

Subject 399—Printing Ink Ordinary Certificate

Mr P. T. Redmond (*Student— Irish*)

Paint Technician's Certificate. Part I.

J. Barrie (*Student—Manchester*)

R. Fox (*Student—Manchester*)

A. Hazlewood (*Student—Newcastle*)

F. J. Hookway (*Student—Thames Valley*)

M. E. Todd (*Student—Manchester*)

A. Whatling (*Student—Manchester*)

Paint Technician's Certificate. Part II.

R. Dunster (*Student—Midlands*)

S. A. R. Hamdulay (*Ordinary— London*)

D. Howell (*Student—London*)

P. C. Neal (*Student—London*)

T. M. D. Shelley (*Associate— Midlands*)

M. Smith (*Student—West Riding*)

C. M. Trueman (*Student—Thames Valley*)

B. D. Yellop (*Student—London*)

British Society of Rheology

The 1971 Autumn Conference of the British Society of Rheology, scheduled provisionally for 20-23 September, will not take a specific title on this occasion but will be of a completely general nature. It is, however, proposed to hold specific sessions on polymers, disperse systems and instrumentation. Papers on these, and any other rheological topic, are invited. Intending authors are asked to communicate their intent, as soon as possible, to

Mr A. Please
Materials Section,
Road Research Laboratory,
Crowthorne,
Berks. RG11 6AU.

Titles and abstracts should be forwarded so as to reach the above address not later than 1 May 1971.

Register of Members

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

Ordinary Members

BERKELEY, ALFRED, BSc, 12 Serpentine Road, Dublin, 4, Ireland.   (*Irish*)

BICKERSTAFFE, TERRENCE, 36 Rayner Street, Horbury, Nr. Wakefield, Yorks.
(*West Riding*)

BINIAS, DEREK, 2 Blackwood Grove, Tinshill Lane, Leeds, 16, Yorks.   (*West Riding*)

COWPER, PETER WILLIAM, 30 Thornbera Road, Bishop's Stortford, Herts.   (*London*)

FENNELL, EDWARD, 33 Oak Street, Romford, Essex.   (*London*)

GADD, ANTHONY RICHARD, BSc, 3 St. Teilo Close, Dinas Powis, Glam. CF6 4TY.
(*Bristol*)

GREENHALGH, MALCOLM, BScTech, BSc, AMCT, 10 Greenton Crescent, Queensbury,
Bradford, Yorks.   (*West Riding*)

MILNE, JOHN ARNOLD, BSc, MSc, 8 Longmeadows Drive, Laceby, Grimsby, Lincs.
(*Hull*)

NETZSCH, WOLFGANG, Dipl. Ing., Siebenbergerstr 8, 8264, Waldraiburg, Germany.
(*Overseas*)

NEWTON, BRIAN, Runnymede Dispersions Ltd., Ruspidge Road, Cinderford,
Gloucester.   (*Bristol*)

OFFERMANS, JACQUES JEAN-MARIE, Ing. Tech. Chimiste, 23 Rue Van Rollegem, 1090, Bruxelles, Belgium.   (*Overseas*)

ROGIRST, ANDRE, Dr in Chem., UCB/Afdeling SIDAC, Ottergems Steenweg, 801, B-9000, Gent, Belgium.   (*Overseas*)

SCHWARTZ, LEONARD STANLEY, 68-04 150th Street, Flushing, New York, 11367, USA.
                                                                                    (*Overseas*)

SIDDLE, GEORGE ROY, BSc, FRIC, 21 Lyndon Way, Louth, Lincs.   (*Hull*)

SIMMONDS, JOHN, 15 William Street, Rainham, Kent.   (*London*)

THOMAS, JOHN HENRY CAREW, 37 Cwm Barry Way, Barry, Glam. CF6 8LA.
                                                                                     (*Bristol*)

WIJNS, EDWARD, Ing. Tech. Chimiste, Hospitaalstraat, 52B, 2648, Steendorp, Belgium.
                                                                                    (*Overseas*)

Associate Members

DILLON, JOHN, Geigy (UK) Ltd., Roundthorn Industrial Estate, Wythenshawe, Manchester.   (*Manchester*)

HEALD, ALAN JEFFREY, 101 Shadowmoss Road, Woodhouse Park, Wythenshawe, Manchester.   (*Manchester*)

KEAY, JOSEPH ASSENTY, 95 Barnes Avenue, Dronfield-Woodhouse, S18 5YR.
                                                                                 (*West Riding*)

ROBIC, EDUARDO JOSE, Juan B. Justo 2331, 7° Piso, 32, Buenos Aires, Argentina.
                                                                                    (*Overseas*)

Student Members

HUNT, MICHAEL ANDREW, 37 Arlington Street, Hull.   (*Hull*)

JONES, EDWARD JOHN, 48 Craddock Street, Riverside, Cardiff, CF1 8EU, Glamorgan, South Wales.   (*Bristol*)

PARLING, WILLIAM GEOFFREY, 154 Hall Lane Estate, Willington, Crook, Co. Durham.
                                                                                  (*Newcastle*)

THOMAS, KENNETH CHARLES, 119 St. Davids' Crescent, Penarth, Glamorgan, South Wales.   (*Bristol*)

Forthcoming Events

Details are given of meetings in the United Kingdom up to the end of the month following publication, and in South Africa and the Commonwealth up to the end of the second month.

Thursday 3 December

Midlands Section—Trent Valley Branch: "Safety in the paint industry" by Dr L. E. Euinton HM Medical Inspector of Factories, to be held at the British Rail School of Transport, London Road, Derby at 7.00 p.m.

Newcastle Section: "Coal tar based surface coatings" by Dr D. McNeil of the Coal Tar Research Association, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle upon Tyne at 6.30 p.m.

Monday 7 December

Hull Section: "The value of gel permeation chromatography for the

design of alkyd resins" by Mr H. Olley and Dr L. A. O'Neill of the Paint Research Station, to be held at the Bullock Lecture Theatre, Hull College of Technology at 7.00 p.m.

Tuesday 8 December

West Riding Section: "Milling—a variable in ink performance" by Mr J. Groom of Sandoz Products Limited. Joint Meeting with the Institute of Printing, to be held at the Griffin Hotel, Boar Lane, Leeds at 7.30 p.m.

Wednesday 9 December

Newcastle Section—Student Group: "Marine fouling" by Dr A. O. Christie

of the International Paint Company Limited, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle upon Tyne at 3.00 p.m.

Thursday 10 December

London Section: "Addition copolymers of the vinyl ester of branched chain fatty acids for use in electrodeposition paints" by Dr W. J. van Westrenen of Koninklijke Shell Plastics Laboratories, Delft, and Mr W. H. M. Nieuwenhuis of Koninklijke Shell Laboratories, Amsterdam; to be held at the East Ham Technical College, High Street South, London E6, at 7.00 p.m.

Scottish Section: "Development of gloss paints in the twentieth century" by Mr I. R. McCallum and Mr M. Devine of P. W. Hall Limited, to be held at the St. Enoch Hotel, Glasgow at 6.00 p.m.

Friday 11 December

Irish Section: "Ladies Night" to be held at the Clarence Hotel, Wellington Quay, Dublin at 8.00 p.m.

Manchester Section: "Chloride titanium dioxide pigments—their value" by Mr J. S. Jordan and Mr F. D. Robinson of Laporte Industries Limited, to be held at the Liverpool Building and Design Centre, Hope Street, Liverpool 1 at 6.30 p.m.

Saturday 12 December

Scottish Section—Student Group: "Surface preparation" by A. Pisacane, of Craig Hubbuck Ltd., to be held at the St Enoch Hotel, St Enoch Square, Glasgow at 10.00 a.m.

Wednesday 16 December

Scottish Section—Eastern Branch: "Modern developments in titanium" by Mr G. Willison, of British Titan Products Limited, to be held at the Carlton Hotel, North Bridge, Edinburgh at 7.30 p.m.

Monday 4 January

Hull Section: "The preservation and waterproofing of joinery timber prior to painting", by Mr R. R. Hill of the Timber Research and Development Association, to be held at the Bullock Lecture Theatre, Hull College of Technology, at 7.00 p.m.

Thursday 7 January

Newcastle Section: "Discounted cash flow and investment appraisal—a management technique", by Mr K. W. Blackburn of the Sunderland Polytechnic, to be held at the Royal Turks Head Hotel, Grey Street, Newcastle-upon-Tyne, at 6.30 p.m.

Friday 8 January

Manchester Section: "Printing inks for web-offset", by Mr D. E. Bisset of Coates Bros. (Inks) Limited, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1, at 6.30 p.m.

Saturday 9 January

Scottish Section—Student Group: "How the alkyd resin replaced the drying oil", by Mr G. H. Hutchinson, of A. B. Fleming & Co. Ltd.

Tuesday 12 January

West Riding Section: "Two-pack epoxy coatings", by Mr A. McKay of CIBA (ARL) Limited, to be held at the Griffin Hotel, Boar Lane, Leeds, at 7.30 p.m.

Wednesday 13 January

Manchester Section—Student Group: "The use of carbon black in paints, plastics and printing inks", by Mr B. E. Thomas of Columbian Industrial Limited, to be held at the Manchester Literary and Philosophical Society, 36 George Street, Manchester 1, at 4.30 p.m.

Newcastle Section—Student Group: "Modern management techniques", by Mr N. D. Harris of the Dept. of Management Studies, Newcastle Polytechnic, to be held at the Newcastle Polytechnic, Ellison Place, Newcastle-upon-Tyne, at 3.00 p.m.

Friday 15 January

Irish Section: "Modern dispersion equipment", by Mr H. Wadham of Torrance & Sons Limited, to be held at the Clarence Hotel, Wellington Quay, Dublin, at 8.00 p.m.

Midlands Section: Annual Dinner Lecture. "Microscopic examination of pigment-vehicle interaction during film formation", by Dr Jettmar and Dr Apel of BASF, to be held at the Winston Restaurant, Birmingham 5, at 6.30 p.m.

Scottish Section: Annual Dinner Dance.

Wednesday 20 January

London Section: Conversazione: "Surface coatings: their use and abuse for painting structural steel" Mr R. Hullcoop of ICI Ltd., Paints Dvn., Mr J. Runham of J. D. & S. Tighe, Mr K. Harden, of W.P.M. Paints Dvn., Mr J. Rogers of Shell International Petroleum Co. Ltd., and Mr R. C. Dent of C.E.G.B., to be held at the Borough Polytechnic at 2.15 p.m.

Scottish Section—Eastern Branch: "Money go round". A 30 minute film and talk on commercial practice by a speaker from the Scottish Stock Exchange, to be held at the Carlton Hotel, North Bridge, Edinburgh, at 7.30 p.m.

Thursday 21 January

Irish Section: Annual Dinner Dance in the Clare Manor Hotel.

Midlands Section—Trent Valley Branch: "The future of water-thinnable coatings", by Mr A. J. Becalick of Lennig Chemicals Limited, to be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Scottish Section: "Handling of solvents", by Mr I. M. Fotheringham of Shell Chemicals (UK) Limited, and "Hazards of solvent fires", by A. D. Officer Clarke of the Fire Prevention Section, Glasgow Corporation Fire Dept. To be held at the St. Enoch Hotel, Glasgow, at 6.00 p.m.

Thames Valley Section: "Special problems of paints and mastics with reference to building techniques", by Mr E. L. French of Taylor Woodrow Construction Limited, to be held at The Beech Tree Hotel, Beaconsfield, Bucks., at 7.00 p.m.

Friday 29 January

Bristol Section: Ladies Evening. "Cosmetics", by Mr A. Foster of Revlon Overseas Corporation, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

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(C)— Correspondence
(D)— Discussion
(E)— Editorial and Comment
(N)— Notes and News
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(SC)— Short Communications
(SR)— Student Review
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copolymer resin	4, 24, 30
emulsion resin	20, 27, 28, 29, 30
epoxy resin	8, 19, 32
melamine formaldehyde resin	8, 43
melamine resin	9
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phenolic resin	8
polyamide resin	19
polyethylene	50
polyethylene glycol	21
polymer	4
styrene resin	30
styrene acrylic emulsion	27
urethane resin	8, 20
Versatate copolymer resin	27
vinyl resin	24
vinyl acetate resin	30
vinyl acetate ethylene resin	22
vinyl copolymer resin	27, 34
vinylidene resin	29
water soluble resin	16

—Prime pigments and dyes

aluminium pigment	9, 44
anatase titanium dioxide	34
dioxazine violet	42
iron oxide pigment	32
phthalocyanine blue	42
pigment green B	42
red iron oxide pigment	3
red lead	44
red lead pigment	9
rutile titanium dioxide	34
titanium dioxide	17

—Chemically active pigments

zinc chromate	3

—Extender pigments

aluminium silicate	52
clay	16
fumed silica	52
precipitated silica	52
pyrogenic silica	52

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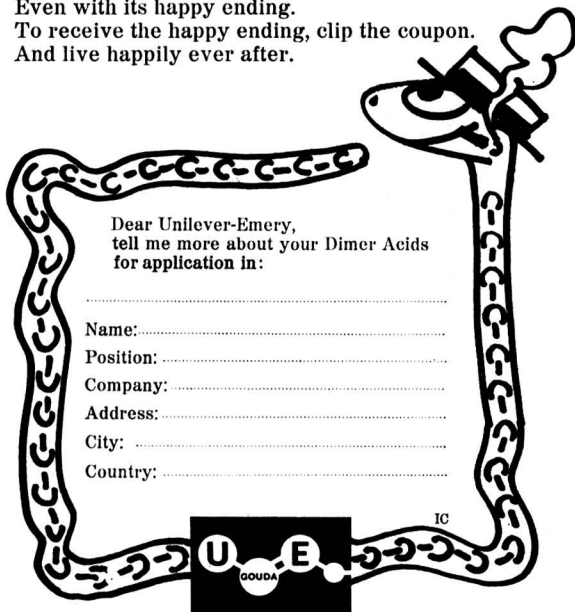
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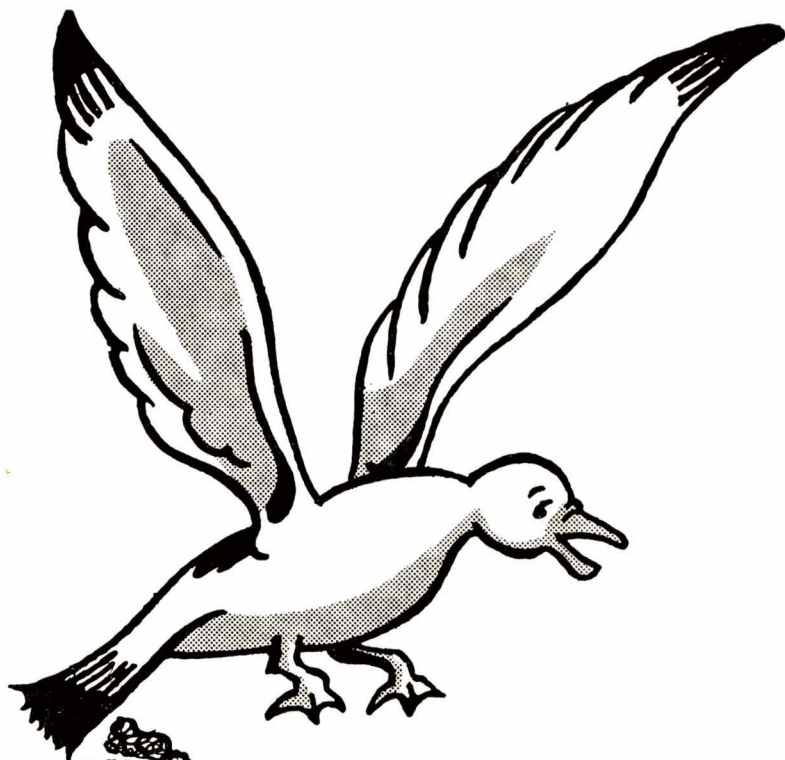
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