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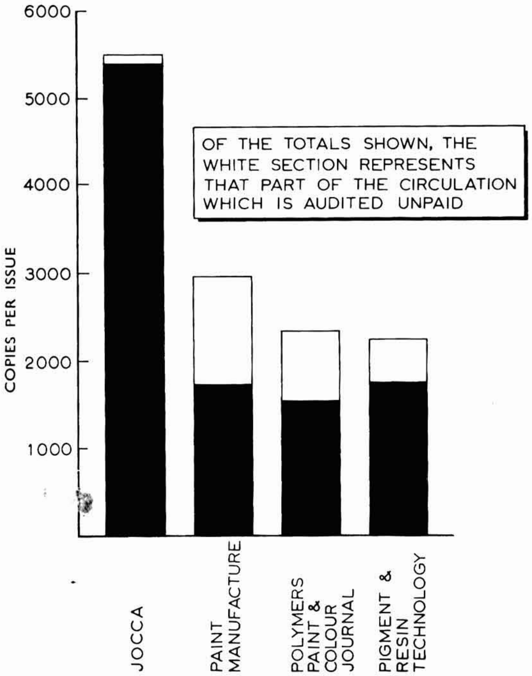

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Transactions and Communications

Some physical properties of pigments
II. The measurement of tensile strength and its development in compacted powders

By M. J. Smith

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Summary

The ease with which pigment agglomerates disperse during mixing with plastics must depend upon their strength. Whilst considerable attention has been, and continues to be applied to the measurement of dispersion, little effort is directed towards determining agglomerate strength. This is most easily accomplished by examining agglomerates outside the polymer matrix.

A wide range of pigment powders has been "agglomerated" using a tableting press, when the initially discrete particles bond together to form a coherent mass with more than sufficient strength to be regarded as a new particle. The tensile strength of the resulting compacts was measured and found to be related to the closeness of packing in the new agglomerate. It was also found to vary with pigment type, although similar pigments showed features in common. All pigments exhibited a range of strengths, varying from the strength of the virtually solid material to the cohesion of the loosely-packed powder. This type of behaviour conforms closely to the Gompertz curve.

The mechanism of agglomeration is examined in detail. The behaviour of the various pigments and the variances found in some of the results are explained.

Keywords

Processes and methods primarily associated with manufacturing or synthesis

agglomeration

Processes and methods primarily associated with analysis measurement and testing

tensile testing

Quelques caractéristiques physiques de pigments
Deuxième Partie: Le mesurage de la résistance à la traction et son développement en poudres compactés

Résumé

La facilité des agglomérés pigmentaires à être dispersés lors du mélange avec les matières plastiques doit se dépendre de la tenacité des agglomérés. Bien qu'on ait consacré des études importantes au mesurage de l'état de dispersion et également que l'on continue à le faire, on n'a pas orienté beaucoup d'effort vers la détermination de la tenacité des agglomérés. On peut effectuer cette détermination dans la manière plus facile en étudiant les agglomérés en dehors de la matrice polymère.

On a produit les agglomérés d'une gamme étendue de pigments en poudre, au moyen d'une presse pour la fabrication de comprimés, où les particules, initiallement discrètes, se lient en produisant une masse cohérente ayant assez de tenacité à être considérée comme une nouvelle particule. On a déterminé la résistance à la traction des compactés qui en résultent et on a trouvé un rapport entre elle et le degré d'intimité de tassement des nouveaux agglomérés. On a trouvé d'ailleurs qu'elle se varie selon le type pigmentaire, bien que les pigments semblables mettent en évidence des caractéristiques communes. Tous les pigments montraient un éventail de tenacités, à partir de celle d'un corps quasi-solide, jusqu'à la cohésion du poudre légèrement entassé. Ce genre de comportement accorde fortement à la courbe de Gompertz.

On étudie, en détail, le mécanisme d'agglomération. On explique le comportement de divers pigments ainsi que la variation de certains résultats.

Einige Physikalische Eigenschaften von Pigmenten
II. Das Messen der Zugfestigkeit und deren Entwicklung in Zusammengepressten Pulvern

Zusammenfassung

Die Leichtigkeit, mit welcher Pigmentagglomerate bei der Mischung mit Kunststoffen dispergieren, muss von ihrer Festigkeit abhängen. Während der Messung von Dispersion erhebliche Beachtung geschenkt wurde und noch geschenkt wird, werden nur geringe Anstrengungen auf die Bestimmung der Festigkeit von Agglomeraten gerichtet. Am leichtesten ist diese durch Prüfung von Agglomeraten ausserhalb der Polymermatrix durchführbar.

Unter Benutzung einer Tablettierpresse wurden Pigmentpulver "agglomeriert," wobei sich die ursprünglich einzelnen Teilchen so miteinander verbinden, dass eine kohärente Masse von grösserer als nur ausreichender Festigkeit gebildet wird, sodass sie als ein neues Partikel angesehen werden kann. Die Zugfestigkeit des entstandenen Presslings wurde gemessen und dabei festgestellt, dass diese in Zusammenhang mit der Dichte der Packung im neuen Agglomerat steht; ebenfalls, dass sie je nach Pigmenttype verschieden ist, obwohl ähnliche Pigmente gleiche Merkmale aufwiesen. Alle Pigmente zeigten einen Bereich von Festigkeiten, welche zwischen den von sozusagen festem Material bis zur Kohesion der locker gepackten Pulver variierte. Diese Art des Verhaltens stimmt eng mit der gompertzkurve überein.

Некоторые физические свойства пигментов.
II. Измерение прочности на разрыв и ее развитие в компактных порошках

Резюме

Легкость с которой пигментные агломераты диспергируются при смешивании пластиков, должна зависить от их устойчивости. В то время как значительное внимание уделялось и все еще уделяется вопросу измерения дисперсности, мало усилий направлено на определение устойчивости агломератов. Это наиболее легко достигается анализом агломератов вне полимерной матрицы.

Проводилась агломерация широкого ряда пигментных порошков применяя табличный пресс, где исходные дискретные частицы соединяются между собой, образуя когерентную массу обладающую достаточной устойчивостью для того чтобы рассматривать ее как новую частицу. Разрывная прочность образуемых компактов измерялась и найдено что она связана с плотностью частиц в новом агломерате. Найдено также что прочность изменяется с типом пигмента, хотя сходные пигменты обнаружили общие характеристики. Все пигменты обнаружили диапазон прочности от прочности фактически твердого материала до когезии свободно упакованного порошка. Подобное поведение хорошо согласуется с кривой Гомперца.

Механизм агломерации подробно рассматривается и дается объяснение поведения различных пигментов и расхождения в некоторых результатах.

Introduction

It is generally agreed that pigment powders contain three basic types of particle, which are distinguished by strength as well as size; the small primary particle or crystallite, with size between 0.01 and 0.5 micron; the aggregate, consisting of crystals firmly adhering to one another; and the agglomerate, which is a cluster of loosely bound aggregates and/or crystals, which may be as much as several millimetres in diameter. A fourth type of particle is sometimes differentiated, the air flocculate, which is easily separated into its components and then re-formed, but which is best viewed as a large, weak agglomerate.[1, 2]

The plastics industry is not troubled by either the primary crystallites or by the aggregates both of which are too small to be seen by the unaided eye, and too small to introduce mechanical defects into mouldings and sections. Only when they interact to produce agglomerates of a relatively large size, do problems begin. The formation of agglomerates occurs spontaneously, or as the result of the application of some outside force such as that which is encountered during handling, and often occurs as a result of using the wrong powder mixing conditions. The use of too much pigment, or the wrong mixer, can result in the formation of agglomerates which are too strong to be dispersed in any subsequent process. A detailed knowledge of pigment powder properties might enable these difficulties to be overcome by the design of processes which suit the properties of the mixture. Such a step would enable the colourist to save pigment, as well as the time which would otherwise have to be devoted to reprocessing the mixture in order to disperse the agglomerates which have been formed.

Since the dispersion of pigment agglomerates is dependent upon the ability of the mixing process to concentrate enough energy upon them to induce fracture, their strength is of considerable importance. The ease of dispersion of a pigment agglomerate is generally inversely proportional to its strength. A knowledge of agglomerate strength characteristics should, therefore, enable a greater insight into pigment dispersion to be obtained.

Very little information is available, as yet, concerning the strength of pigment agglomerates[3, 4] although considerable work has been reported relating to particles in general[5–11], and small particles in particular.[12–14] Work has also been reported of measurements of the strength of powders in bulk while subjected to low levels of stress.[15, 16]

Some attempts have already been made to measure the strength of pigment agglomerates directly.[17] Agglomerates were produced by compacting pigment powders in a pharmaceutical tableting machine, and changes in pressure followed by means of strain gauges. It had been expected that the residual pressure supported by the agglomerate in the die wall would, after removing the punch, be a measure of that agglomerate's strength. Unfortunately, the expectation was frustrated by the agglomerate being elastic and therefore able to deform so as to release this pressure. Hence it was concluded that a more direct route was necessary. This paper describes the compaction of powders to produce agglomerates in the form of tablets which were subsequently stressed to rupture across a diameter.

Experimental

Apparatus

In this second attempt to measure particle strength, pigment powders were compressed in the same single-stroke Manesty F3 pharmaceutical tableting machine, as has already been described.[17] By varying the quantity of pigment placed in the die, but keeping the machine settings constant, tablets of varying thickness and density were produced.

Two different methods were considered for measuring the strength of these tablets. The first involved application of a simple tensile stress along the direction of compression by means of a "Tensometer".[6] Two metal surfaces were bonded on to the tablet, care being taken to avoid a direct metal-metal link by the adhesive, either round the edges or through the body of the tablet when it was porous. For obvious reasons this method of stressing the tablet was both slow and tedious.

The alternative method involved stressing the tablet to rupture across its diameter.[8] It has been shown that under these conditions, failure will occur along the diameter whilst the material is in tension across it. This method of measuring tensile strength has been extensively used for general[9, 10] as well as pharmaceutical[18–20] studies; but recent work has shown that for representative results to be obtained the tablet must break such that the major stress is tensile.[19]

Under conditions of line loading, as occur with tablets that are hard or have a high elastic modulus, both shear and compressive forces are generated. These are minimal at the centre of the load diameter and very high immediately under the load points. The presence of these high stresses will prevent the initiation of failure in tension.

In practice, ideal line loading will never occur owing to the deformation of the load points with the subsequent distribution of the load over a greater area. It is thus possible to approach a condition where tensile stress is constant over most of the load diameter and the shear and compressive stresses have been greatly reduced. In this state, failure is initiated with the sample in tension. Such a condition can be achieved most satisfactorily with soft tablets, or in the case of hard materials by placing a narrow pad of soft material between the tablet and the plattens.[20, 21]

In this experimental work a Pfizer hardness tester fitted with blotting paper pads was used to measure the crushing strength of the tablets. This instrument, which is widely used in the pharmaceutical industry, suffers from the disadvantage that its rate of loading is not necessarily constant, and that its sensitivity is low at small loadings.

Tensile strength was calculated using the following relationship.

$$\text{Tensile strength} = \frac{2W}{\pi L D}$$

Where W is the applied load
L is the tablet thickness, and
D is the tablet diameter.

The values of tensile strength so obtained were compared with the compaction produced in the tablet. The level of compaction, expressed as the voids ratio, was obtained by comparing the bulk density of the tablet with the ultimate density of the pigment particle (its specific gravity) using the formula:

$$\text{Voids ratio} = \frac{\text{ultimate density—bulk density}}{\text{bulk density}}$$

Sources of error

It was possible to distinguish two principal sources of error that arose in this work; uneven packing in the die prior to compaction, and uneven breakage of the tablet when it was crushed (which has already been described).

Uneven packing arose owing to the tendency of the powders to form heaps and to fill the tableting die unevenly when it was loaded by hand. Attempts were made to counteract this by redistributing the heaps as much as possible with a spatula, but this operation was difficult to accomplish, especially when the pigment level was below the top of the die. In fact no completely satisfactory solution was found to this problem, although adequate care and attention during filling did much to overcome it.

A third possible source of error could have arisen in this work because the conditions under which a powder is compacted control the nature of the agglomerate produced. As pharmaceutical tableting machines are, in general, not very well calibrated, it would have been difficult to re-create the identical situation once machine settings were disturbed. However, this problem was anticipated, and the comparisons between pigments were all made under identical conditions.

Agglomerating mechanisms in pigment powders

Agglomerates, which are permanent entities possessing measurable strength, are often formed contrary to intention during the handling of pigment powders. There are many factors which encourage their formation, such as the presence of moisture and the application of pressure and/or heat. Agglomeration can often occur under quite mild conditions of handling, as for example during storage. During conveying or mixing, it will occur much more easily; whilst the mechanical agitation of carbon blacks in a high speed mixer, or of zinc oxide in a tumble mixer[3] will tend to form comparatively dense, strong agglomerates.

There are obviously two related mechanisms which are critical to the development of agglomerates; that by which small particles take up a closely packed structure, and that by which adhesion forces are developed between them so as to produce a structural strength.[22]

Compaction

It is agreed unanimously in the literature that the initial mechanism of compaction is one of rearrangement, where the particles are forced to slide over, and between one another. The finer the initial subdivision of the powder, the lower is its bulk density and the greater is the opportunity for rearrangement. For example, uncompacted titanium dioxide can be so fine, and consequently its volume so great, that only one sixth of its apparent volume is occupied by the pigment particles.[23] The low bulk density and high voids content of these fine powders is dependent upon the relatively large interparticle forces in relation to particle mass. These small particles will have, proportionally, a much greater force holding them in equilibrium position.

As particle size increases, the powder becomes much less able to support this extra volume and the particles approach one another more closely. The relatively low voidage of these coarse powders allows very little opportunity for rearrangement to take place during compaction, almost preventing this mechanism from being brought into play.

Whatever its apparent density, however, the loose powder can only support a small stress before it has to deform. The first small deformation is elastic, but thereafter the powder structure fails and rearrangement follows until the stage is reached where the amount of space is greatly reduced. Thereafter each successive rearrangement pushes the particles closer together, and makes the compact stronger and therefore more resistant to subsequent deformation.

The gradual increase in bulk density upon compaction can be divided into two stages. The first is simple rearrangement, which is characterised by an unchanged, or only slightly modified, particle size distribution. The second stage is associated with the filling of those voids which are substantially smaller than the surrounding particles. These voids can be filled only by flow or fragmentation. It is generally agreed that three possibilities exist—elastic deformation, plastic deformation, and fragmentation. These are concurrent, rather than separate, possibilities.[24]

Very little evidence has yet appeared to allow a relative importance to be assigned to these different mechanisms, or even to relate them to the behaviour of specific materials under compaction. Some materials which are generally regarded as brittle behave plastically when the particles are small and subjected to high stress. Hardman and Lilley[25] have found that the densification of sodium chloride involves plastic deformation, whereas for sucrose, fragmentation of the original particles occurs. Coal, which has been studied extensively,[26–28] appears to be intermediate between these two extremes. The involvement of the two mechanisms (deformation and fragmentation) has been confirmed, and a method developed whereby they may be distinguished. This involves plotting a function of the relative density of the agglomerate against the applied stress according to an equation derived by Heckel.[29] Differences may be seen in the resulting graphs according to which mechanism is involved. Evidence has also been produced[30] to suggest that quartz powders compress normally (i.e. rearrangement and fragmentation) up to stresses of 20,000 psi, but that above this an element of elastic deformation appears amounting to about 5 per cent of the total deformation.

The speed with which compressive forces are applied to the powder must also influence the packing produced. For example, if the compacting stress is applied rapidly, the powder will be unable to flow or to undergo plastic deformation. Fast compaction will allow little time for rearrangement to occur before the compacting stress is removed; and because the particles on the outside of the tablet are subjected to greater stress, differences in density throughout the compact will increase, leading to internal strain. Slower compaction will allow particles more time to deform, relieving pressure and increasing strength. It may also permit the escape of air[31] thus producing a more robust compact.

With uniaxial compression, such as that used for the manufacture of tablets, friction between the powder particles and the die wall will induce shearing forces within the powder, particularly at the surface of the tablet and, unexpectedly, quite often in its lower mid-centre.[31] In contrast, the interior of a powder during bulk storage (and perhaps during use) is not subjected to these conditions, and the packings which are produced are more likely to be even. The particles at the bottom of the pile remain undisturbed and will agglomerate as a result of compaction. Those within the heap will agglomerate by a variety of mechanisms including frictional bonding and static forces, whilst at the surface of the heap particles may be adversely affected by the absorption of moisture.[32] The conditions within a mixer will be much more complex than this.

Coherence between particles

The stability of an agglomerate is dictated not only by the way in which the particles are packed, but by the nature of the interaction between them. Many suggestions have been made as to the nature of this bonding, in particular by Rumpf[6] and his co-workers, and these are discussed below.

Particle interlocking

A three dimensional structure is produced which leaves the particles with sufficient strength to resist the disruptive forces resulting from elastic recovery when the compacting stress is removed.

Friction and compression welding

At point contacts, welding results from localised heating during compactive rearrangement. This has been observed in a variety of powders, ranging from sulphur and milk powder,[23] to lactose and griseofulvin, a pharmaceutical product,[35] and is easy to appreciate. Harwood,[33] examining the effect of temperature upon bulk density, cohesion and tensile strength for a number of powders, has shown that the lowering of the melting point of the solid which arises from increased pressure is considerable. For example, calculations based on the equation derived by Shotnicky[16] from the classical Clausius-Clapeyron equation predict a lowering of 0.29°C per atmosphere for the melting point of griseofulvin.

Bowden and Tabor[34] have suggested that the real area of contact between particles in a powder is in the order of 5×10^{-4} of the apparent surface area, and Rankell and Higuchi[35] agree with this, placing it between 10^{-3} and 10^{-4} of the apparent surface area. Thus even for relatively low loadings during compaction, such as 300 g cm^{-2}, the actual stress at the point of contact can approach 600 atmospheres. Such a high loading will certainly affect the melting point, and for griseofulvin it will be reduced from 220° to about 40°C.[33] This is in close agreement with earlier work,[16] where the melting of point contacts in griseofulvin occurred at 65°C.

It has been shown[36] that in the manufacture of tablets, considerable energy is expended during compression. Assuming that all this energy appears as heat, the resulting rise in temperature could be as much as 5-20°C. In practice, temperature rises of 10.4-14.0°C have been recorded for griseofulvin,[37] and using a more direct method, where tablets were immediately transferred to a microcalorimeter, temperature rises of 11.5°C were recorded.

This figure is clearly an average temperature rise, since at the actual points of interparticle contact the rise will be considerably higher, especially for short compaction times. As described above, this localised heating and melting will enable the points of contact to become welded together upon cooling; and cooling will take place almost immediately since the bulk of the material in the tablet is still at room temperature.

It is not difficult to imagine localised pressures of this sort arising during mixing, and since a large number of the pigments currently used for colouring plastics are especially treated with surface coatings of an organic nature they are open to pressure sintering of this type. This is especially true for the inorganic pigments which, being refractory, do not themselves melt under pressure. For example titanium dioxide does not melt until the temperature reaches about 1800°C, and therefore if pressure sintering does occur melting is much more likely because of the presence of a surface coating.

Bridging

Solid bridges between particles may be formed by mechanisms other than fusion. These include solid diffusion, chemical reaction, and the setting of binders,[10, 11] as well as the crystallisation and sintering of reaction by-products. Liquid bridges[6, 32, 38] must also be considered in the case of contamination or when pigments have hygroscopic coatings.

Van der Waal's forces

These contribute significantly to the development of agglomerate strength once the particles have been brought close enough together ($\leqslant$ 5Å).

Electrostatic forces

Electrostatic forces can contribute significantly to the strength of the powder while it is still relatively loosely packed. Interparticle attraction is proportional to the area of contact and is, therefore, most effective when the particles are of varying sizes, or when some of them are soft and can deform. Both of these conditions are satisfied by modern pigments which have a wide range of particle size, and are frequently surface treated with materials of an organic nature which deform relatively easily.

Mechanical strength of compacted agglomerates

The coherence of particles, arising from pressure compaction or other forms of agglomeration, has been extensively studied by Rumpf.[6] The type of interparticle bonding, as well as the closeness of packing, determines the ultimate strength of the agglomerate. The relationship between strength and voidage has been examined for a number of materials, including coal,[9] sucrose,[18] and zinc oxide.[3] In all cases, strength was found to be a single valued function of porosity as well as being dependent upon the size of the compact. Several different relationships have been put forward.

For powdered coal, a curve was obtained which followed the general equation

$$\text{Strength, } S = K\,(1\text{-}\bar{p})\,\bar{p}^{-1}$$

where K is a numerical constant having the dimensions of stress and p is porosity.

Sucrose was found to follow an empirical relationship originally derived for ceramic materials.[38]

$$S = S_0\, e^{-b\bar{p}}$$

where S_0 is the crushing strength at zero porosity and b is a constant.

Unfortunately, no direct comparison can be made between these two curves since the compacting stresses are not fully quoted.

Zinc oxide agglomerates produced under low compacting stresses such as those found during tumbling in a rotating drum, were found to follow the equation

$$\frac{S}{d^2} = K\,\varphi\, e^{7\cdot 2}$$

where d is the diameter of the spherical agglomerate and φ is the volume fraction of solids.

None of the functions outlined above provide a close description of the type of curve obtained in these experiments; they conform more closely to the type of curve known as "Gompertz." This is a curve much used in statistical work to describe the growth of natural populations and demands, and its form is given by the equation

$$Y = Ka^{b^{x}}$$

where K, a, and b are constants, Y is the voids ratio and x is the strength of the compact. This equation exists in four different forms depending upon the values assumed by the various constants. That which best fits the data shown in Figs. 1-12 is obtained when log a is negative and $b < 1$. Constant K then assumes the value of the upper limit of strength, shown by the compact at zero voids content.

Tensile strength has also been related to the compacting stress which produces it,[19, 20] when pharmaceutical materials were found to give a straight line. Extensions of this work have related compaction to other mechanical properties such as hardness and porosity.[40]

Many attempts have been made to formulate a method of calculating the strength of a brittle compressed solid.[41] Rumpf,[6] for example, has calculated the strength of agglomerates composed of monosize spherical particles for two types of packing; one in which localised bonding occurs between particles, and the other in which a considerable quantity of binding material is present. All these "theoretical" strengths have been found to be too high.

It is unlikely that the measured tensile strength of an agglomerate produced by compaction will ever reach the upper limit of strength shown by the material itself, for the presence of voids, impurities (intentional or otherwise), uneven packing and the resulting strains, and surface flaws and cracks will all lower its strength. The final measured strength depends largely upon the orientation of the largest flaw, which will extend under stress owing to concentration of the stress at its tip, and thus allow premature fracture of the compact.[12,13]

Bulk density

The bulk density of a powder may vary between wide limits, and those physical attributes which determine it include particle size and size distribution; particle shape; surface characteristics, including the chemical nature and physical form; absorption on to the surface; cohesion and adhesion; previous history including separative or compactive forces and their time and duration; and static charges.

A powder of low bulk density is not stable and settles under the influence of gravity until a new equilibrium is achieved, at which point the compacting forces arising from the mass of the individual particles are just balanced by those of repulsion. In this state, the powder bed will exhibit relatively low strength; but further compaction, arising from increased quantities of pigment, or even from vibration and tapping (such as is experienced during transit) will increase both the bulk density and the strength of the bed. The compaction process can be expected to continue as the load increases until eventually the bulk density of the bed approaches the specific gravity of the material concerned. The greatest strength which these compacts exhibit must be that of the material from which they are made.

Results and discussion

In this study of the strength of pigment agglomerates, a total of 43 pigments were examined by compacting them under a range of pressures up to a maximum of 100 kg mm^{-2}. The pigments formed two groups; one covering as wide a range of different types as possible; the other comparing similar chemical types obtained from different manufacturers, which might be reasonably assumed to be made in different ways. Tensile strength was plotted against voids ratio to produce the graphs shown in Figs. 1-12.

Group 1 (Figs. 1-8)

1. Elf 75, a medium flow channel black (*Cabot Carbon Ltd.*)
2. Black Pearls 83, a densified, granulated channel black (*Cabot Carbon Ltd.*)
3. Polymon Blue LBS, a full shade α-form copper phthalocyanine (*ICI Organics Division*)
4. Cobalt Blue 6305 (*Blythe Colours Ltd.*)
5. Ultramarine Blue M 6925 (*Reckitts Colours Ltd.*)
6. Turkey Red Oxide R27 (*Golden Valley Colours*)
7. Polymon Green GN500 (*ICI Organics Division*)
8. ED Polymon Green GN (*ICI Organics Division*)
9. Polymon Green GS (*ICI Organics Division*)
10. Polymon Green YS (*ICI Organics Division*)
11. Chromium Oxide: W grade (*Associated Chemicals*)
12. Cadmium Deep Yellow P543 (*Blythe Colours Ltd.*)
13. PV Fast Red E3B, a quinacridone (*Hoechst*)
14. Rubine Toner 2BS (*ICI Organics Division*)
15. Cadmium Red P436 (*Blythe Colours Ltd.*)
16. Cadmium Light Red 6785 (*Blythe Colours Ltd.*)
17. PV Fast Red B (*Hoechst*)
18. Cinquasia Violet R: RT-791-D, a quinacridone (*Du Pont*)
19. Kronos RA 41 (*Kronos Titanium Ltd.*)
20. Tioxide R-SM (*Tioxide International*)
21. Microlith Yellow 2G-T (*CIBA-GEIGY*)
22. Cadmium Orange DC 2175 (*Blythe Colours Ltd.*)
23. Yellow Oxide BC (*Reckitts Colours Ltd.*)
24. Irgalite Yellow WSC (*CIBA-GEIGY*)
25. Irgalite Yellow WSR (*CIBA-GEIGY*)
26. Irgafiner Yellow E2 (*CIBA-GEIGY*)
27. Chromophtal Yellow 3G (*CIBA-GEIGY*)
28. Microlith Yellow 3G-T (*CIBA-GEIGY*)

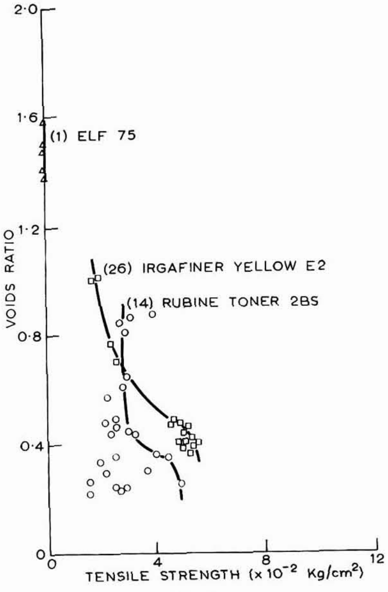


Fig. 1.

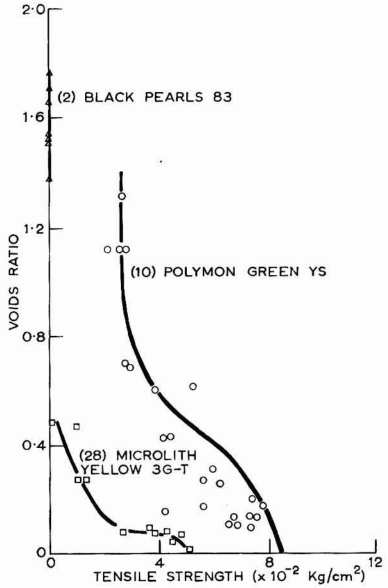
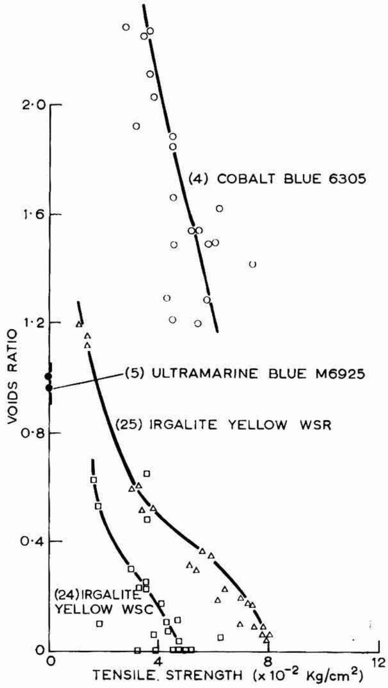


Fig. 4.



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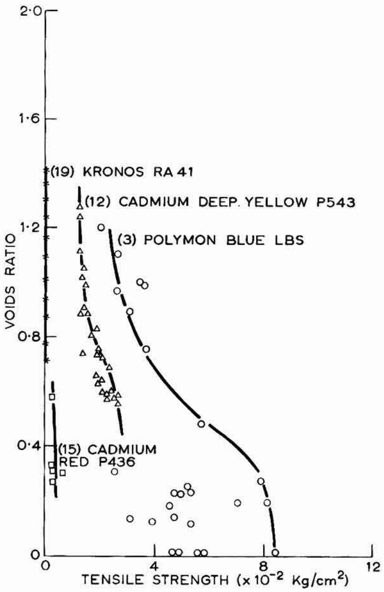
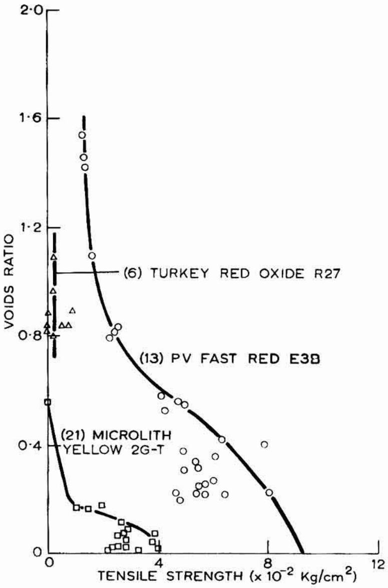


Fig. 3.



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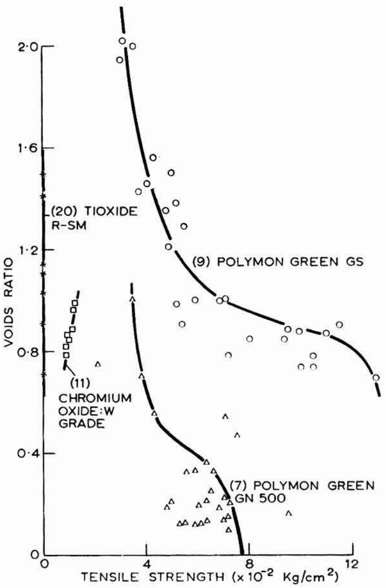

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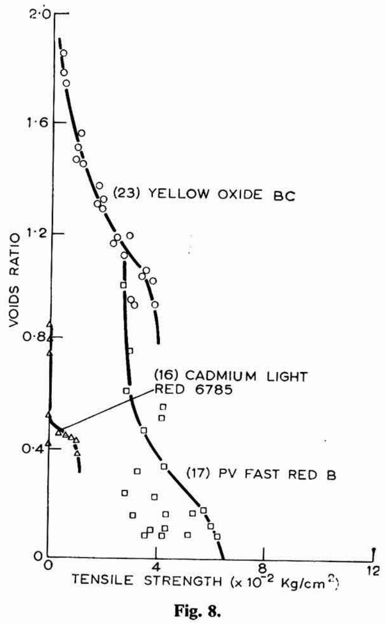

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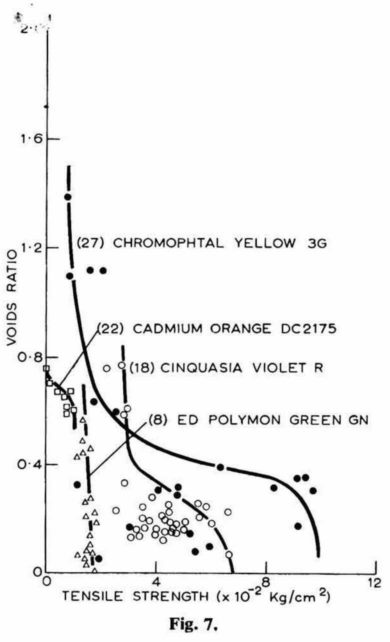

Fig. 7.

Group 2 (Figs. 9-12)

(*a*) *Blue phthalocyanine pigments:*

29. Cyan Blue Toner GT 3000 (*Cyanamid*)
30. Fastona Blue RFR 455 (*SCC Ltd.*)
31. Heliogen Blue BG (*BASF*)
32. Monastral Fast Blue BG (*ICI Organics Division*)

(*b*) *Quinacridone pigments:*

33. Cinquasia Red B (*Du Pont*)
34. Cinquasia Red Y (*Du Pont*)
35. PV Fast Red E5B (*Hoechst*)
36. Quindo Magenta E 16527 (*Harmon*)

(*c*) *Lead molybdate red:*

37. Krolor Red KR-980 (*Du Pont*)
38. Vynamon Scarlet YS (*ICI Organics*)
39. Vynamon Scarlet YS (dedusted) (*ICI Organics*)

(*d*) *Lead chromate yellow:*

40. Krolor Orange 786 (*Du Pont*)
41. Krolor Yellow 787 (*Du Pont*)
42. Supra Fast Middle Chrome GS (*ICI Organics*)
43. Supra Lemon Chrome 4GS (*ICI Organics*)

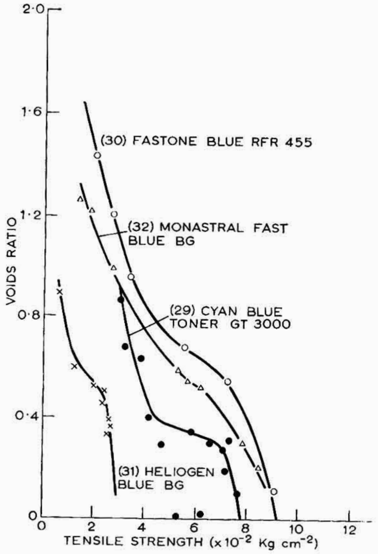

Fig. 9.

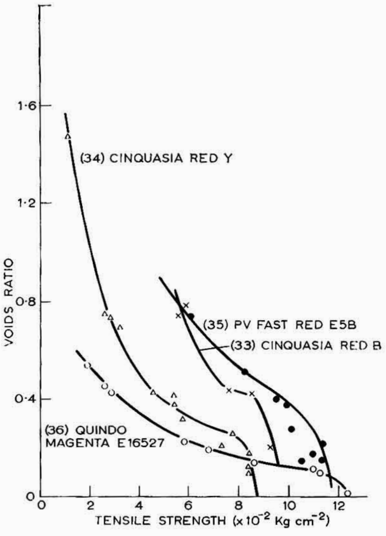

Fig. 10.

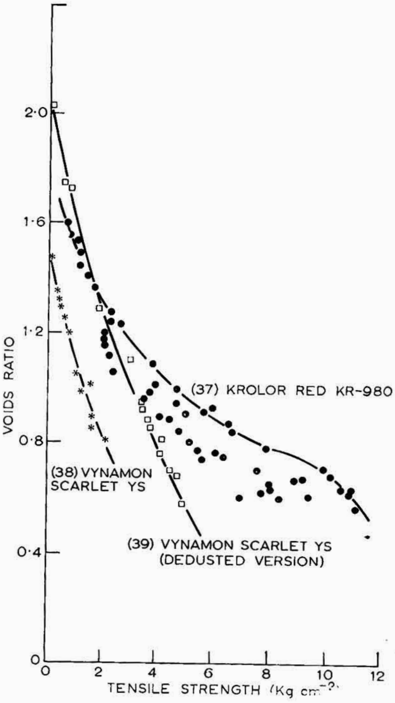

Fig. 11.

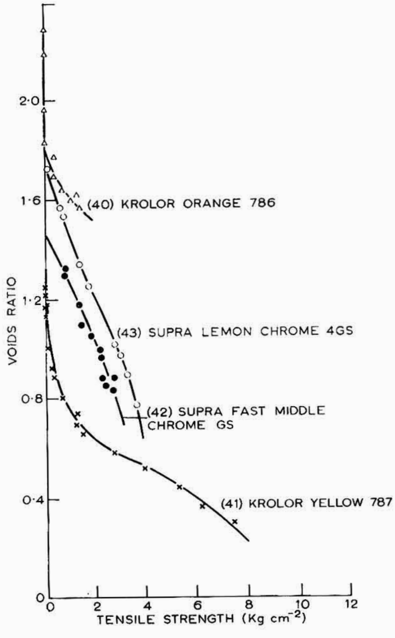

Fig. 12.

Pigment behaviour

Comparison of pigment types

There is a marked difference in behaviour between the inorganic and the organic pigments; the latter are, in general, easily compressed into an agglomerate with a low voids ratio. As a result, the organic tablet quickly develops strength even under comparatively low loadings, and this process continues over a wide range of compactive stress. As would be expected, the most elastic pigments (especially the phthalocyanines[17]) exhibit the greatest range of level of strength. In comparison, the inorganic pigments show much lower levels of compressibility and strength, although there are exceptions to this, for example some of the lead chromates, cobalt blue and yellow iron oxide. This unusual behaviour suggests the presence of a soft organic coating or some other pretreatment.

It is noteworthy that in these tests carbon black behaves as though it were an inorganic pigment, although the reasons for this are by no means clear.

Whilst most inorganic pigments fail to develop more strength than is sufficient to retain the shape of the compact, some cap upon ejection from the die (that is, break across a diametral plane) due to excessive friction on the die wall.[44] Both titanium dioxide and carbon black behave in this way, and the hardness of the pieces remaining suggests that relatively strong tablets developed in the die. The reasons for these primary differences in behaviour between inorganic and organic pigments is not yet clear. They undoubtedly include particle size, size range, and mechanical characteristics, such as shape. The particle size of organic pigments is much smaller than it is with the inorganics, and the particles will be much lighter. This means that the influence of interparticle forces of repulsion will be correspondingly greater, and organic pigment powders will be more fluffy and possess larger voidages. Such a powder system, when compressed, will contain greater opportunities for compaction, and especially for particle rearrangement. By this means the particles can come closer together and a greater number of interparticle contacts will be developed, which will in turn lead to greater agglomerate strength.

The general refractory nature of inorganic pigments renders them much less likely to melt at point contacts when the powder is subjected to compaction. In contrast, the organic pigments may well melt relatively easily, allowing greater compaction and the development of agglomerate strength due to the spot welding. This generalisation is upset, however, by a growing proportion of both organic and inorganic pigments being surface treated. These surface coatings are organic in nature, and able to assist in the development of solid bridges.

Powder systems exhibit a range of strengths, ranging from that of a loose fluffy powder, to that of the solid material devoid of flaws and imperfections. The limits of strength will be approached asymptotically and thus, at some intermediate level of compaction, a point of inflection will occur. This was observed in the work described, and, as can be seen in Figs. 1-12, often occurs at voids ratios between 0.4 and 0.8; but there are some notable exceptions among the inorganic pigments. The inflection also appears to be more sudden, and to occur at a higher voidage, for the inorganic than for the organic pigments.

Similar pigments from different manufacturers

A wide variation has been found between different versions of the same chemical type of pigment. This is probably due to the varying nature of the manufacturing route, especially the final surface treatment. For example, the addition of a de-dusting treatment to a red lead chromate preparation (samples 38 and 39) considerably increased the strength of the compact (Fig. 12). This can be seen at all levels of compaction. The treatment of ultramarine blue with silicone fluid to reduce moisture uptake[4] adversely affects the particle size distribution in the powder (by introducing agglomerates) and increases the possibility of agglomeration by interparticle bridging.

Comparison of the different phthalocyanine blues in Fig. 9 shows that they vary considerably in their strength potential. Now it is to be expected that the strength of an agglomerate will determine the case with which it is broken, and will, therefore, have some bearing upon its dispersibility. A later paper will demonstrate the relationship between these two variables.*

The spread of results

The level of repeatability which might be expected in this type of experiment is difficult to establish since it is virtually impossible to produce two tablets which are identical. Whilst it is possible to make tablets of similar size and density, it is not possible to make them in such a way that they have identical faults. The wide spread of results obtained suggests that variations arising from cracks and fractures are more likely to occur with some pigments than with others; compare Rubine Tower 2BS and Irgafiner Yellow E2 in Fig.1. The incidence of faults, which cause incipient failures of this type, seems to increase with increasing strength and strength range.

The Griffith theory of crack propagation[42, 43] considers a fracture occurring at the "worst" orientated flaw in the surface of the material. The crack extends, under the application of stress, due the concentration of this stress at the apex of the flaw. This theory could explain the large variation in experimental results as it is unlikely that flaws will be identical in an otherwise identical specimen.

Since the presence of flaws can only weaken the specimen, the true relationship between strength and compaction has been shown by a curve drawn through those points showing the greatest strength, whilst points of lower strength have generally been ignored.

Conclusions

A method has been developed using equipment which is normally employed in the pharmaceutical industry to determine the strength of large pigment agglomerates. These agglomerates were produced in the form of tablets which were then crushed across a diameter in order to determine the tensile strength of the material. This provides a method whereby it may be possible to predict the tendency for pigments to agglomerate during handling and in the early stages of mixing with plastic materials.

The ease with which pigments agglomerate under pressure, and the strength of the resulting agglomerates, are the prime causes of the difficulties encountered when plastic materials are coloured by mixing them with pigment.

Large differences have been found to exist between the compactibility and compaction strengths of inorganic and organic pigments. The way in which strength develops with increasing compaction has been correlated with a

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*See page 165.

number of equations derived experimentally, and a new relationship proposed. This takes the form of an equation derived by Gompertz to describe growth phenomena in natural systems.

A comparison has been made between the same chemical type of pigment obtained from several manufacturing sources. Major variations have been found to exist in both the level of strength developed, and the way in which it is related to compaction.

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Some physical properties of pigments
III. The rate at which agglomerates disperse during mixing into plastics

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Summary

It is possible to calculate, from measurements of the particle size distribution of a pigment, a single number which is representative of the rate at which that pigment disperses during mixing. By this means, the dispersing characteristics of a range of different pigment types may be readily ascertained, together with their response to changes in mixing conditions. As might be expected, a considerable difference may be observed between the behaviour of different pigment types. These differences are discussed and related to the physical properties of the pigments concerned.

Keywords

Processes and methods primarily associated with manufacture and synthesis

dispersion

Quelquos caractéristiques physiques de pigments
Troisième Partie: La vitesse de dispersion des agglomérés lors de leur incorporation en matières plastiques

Resume

A partir des mesures de la granulométrie d'un pigment, il est possible de calculer un chiffre unique qui représente la vitesse de dispersion de ce pigment lors du procédé de mélange. Par ce moyen on peut déterminer facilement les caractéristiques d'une gamme de divers types pigmentaires, ainsi que leur comportement à l'égard des changements de conditions de mélange. Comme on doit s'y attendre, il est possible de noter une différence importante entre le comportement de différents types pigmentaires. On discute ces différences et les met en rapport aux caractéristiques physiques des pigments mentionnés dans l'exposé.

Einige Physikalischen Eigenschaften von Pigmenten
III. Die Geschwindigkeit, mit welcher sich Agglomorate beim Einmischen in Kunststoffe Dispergieren

Zusammenfassung

Es ist mit Hilfe von Messungen der Teilchengrössenverteilung eines Pigmentes möglich, eine einzelne Zahl zu berechnen, welche die Geschwindigkeit vorstellt, bei welcher dieses Pigment beim Mischvorgang dispergiert. Die Dispergierungscharakteristika einer Anzahl verschiedener Pigmenttypen können auf diese Weise zusammen mit ihrer Empfindlichkeit gegen Wechsel in Mischbedingungen einfach festgestellt werden. Wie zu erwarten, können erhebliche Unterschiede zwischen dem Verhalten verschiedener Pigmenttypen beobachtet werden. Diese Unterschiede werden besprochen und auf die physikalischen Eigenschaften der betreffenden Pigmente bezogen.

Некоторые физические свойства пигментов.
III. Скорость дисперсии агломератов при смешивании пластиков

Резюме

Из измерений распределения размера частиц пигмента, возможно вычислить число отражающее скорость дисперсии с которой этот пигмент диспергируется при смешивании. Этим образом можно легко определить дисперсные характеристики ряда различных пигментов и также реакцию этих пигментов к изменениям в условиях смешивания. Следует ожидать что значительная разница будет обнаружена в поведении разных типов пигментов. Эти разницы обсуждаются и связываются с физическими свойствами анализируемых пигментов.

Introduction

The rapidity with which a pigment disperses during mixing, together with its stability to weathering and heat, are the principal requirements to be satisfied before it is used in a plastic material. Poor dispersion is unacceptable for a number of reasons. It is a waste of an expensive raw material if more pigment must be used to achieve the required colour; the presence of large particles can lead to electrical or mechanical failure, and in later fabrication stages can lead to the production of specks and streaks; and finally irreproducible dispersion, which results in uncontrolled colour development, removing all hope of easy colour matching. These difficulties can normally be avoided only by reprocessing the mixture, an operation which is both expensive and time consuming.

There is understandably a widespread desire to improve pigment dispersion levels by the modification of machinery and processes. There are also obvious advantages to be gained from using pigments in their standard form, since they are readily available and easily transported; and being simple to handle, they are suitable for the dry colouring process which is widely practised in the plastics industry. Unfortunately, the modification of compounding machinery is of limited practicality due to the high level of capital investment in modern industry.

Pigment dispersion and mixing

If pigments are to be used efficiently, more information about their behaviour in a dispersing environment is required. Several attempts have already been made to devise methods of measuring the quality of dispersion and the way it changes with mixing. Most of this effort has centred on the "tinting strength" test, although a method based upon particle size analysis has recently been developed for studying aqueous dispersions.[1]

The "tinting strength" of phthalocyanine blue in a white paint base has been shown to be directly related to its particle size.[2, 3] This provides a technique which may be applied to plastic media,[4] in which a standard white base is mixed with the pigment being examined. The resulting depth of shade, or "tinting strength," is proportional to the level of dispersion of the coloured pigment. A comparison is usually made between the sample in question, and one or more controls, which were made under conditions especially chosen to give high or low dispersion. For an exact comparison of shades spectrographic curves should be used, but direct colourimetric measurements are usually sufficiently precise to be used on most occasions.[1]

There are, however, a number of associated problems. The level of dispersion can have a pronounced effect upon the shade of the final colour and upon the transparency of a coloured pigment. Since the amount of light scattering undergoes such a great change, a large excess of white pigment is always used, in order that the total amount of scattering should remain almost constant. It is assumed that this pigment remains unaltered during subsequent processing. Finally, large coloured pigment particles appear as nearly black specks in the mixture and therefore make only a small contribution to the final colour.

There are other methods by which the size characteristics of pigment particles may be examined[5, 6] (such as elutriation, sedimentation and sieving) although most of them are rendered useless by the presence of the solid polymer matrix which surrounds the particles in plastics. This leaves the use of the microscope, and this instrument has been used in the past, despite the inherent tedium and subjectivity which is normally associated with it. The recent appearance of automatic particle counters has largely removed these objections, and has assisted in the development of procedures which count and size particles at high speed. There are several of these particle counters currently available, but only the "Quantimet"[7] has achieved any wide acceptance.

Whilst many attempts have been made to study pigment dispersion, most of them have been restricted to the fields of paint and printing ink, and few relate to plastics media.[8] Irrespective of the medium used, dispersion levels have been shown to improve with increasing mixing energies. These are normally achieved by increasing the power or the speed of mixing,[9, 10] but they may also be accomplished with longer mixing times.[11, 14]

Two components are necessary to describe any mixing process, the "dispersion" of large agglomerates into smaller particles, and the "distribution" of these smaller particles throughout the polymer mass to produce a homogeneous mixture. These two separate processes must not be confused, and throughout this paper they will continue to be used in the sense defined here.

Studies of processes which mix pigments and plastics together have generally excluded the size reduction mechanism from consideration, but these two types of mixing invariably occur together. Moreover, by the nature of their interrelationship, dispersion must be the rate controlling step. Dispersion generally occurs due to the action of the shear stresses developed in the polymer, which rupture the agglomerates. When these stresses (the magnitudes of which are determined by the viscosity of the polymer and the mixing conditions) are greater than some threshold value (which will depend upon the characteristics of the agglomerate), dispersion will take place. If the stresses are smaller than are required to overcome the strength of the particle, then it will not be dispersed.

A knowledge of the rate at which agglomerates disappear during dispersive mixing is of great practical value, for it then becomes possible to anticipate problems, and to select or design processes which will achieve optimum dispersion at minimum cost. Also, the total effort required to achieve satisfactory dispersion may be reduced by concentrating upon those pigment which are least easily dispersed.

Changes in the extent of dispersion can generally be followed by measuring the number and size of the particles present. But size analysis of this nature produces a large quantity of data, and comparisons can only be made easily between samples if this quantity is reduced, and preferably reduced to a single number. Several methods by which this may be achieved have already been described.[1, 5]

Dispersion expressed as a single number

Dispersion is an exponential disintegration process analogous to radioactive decay. The amount of dispersion taking place at any time, i.e. the rate of dispersion, depends upon the number of dispersible particles present, their strength, and the maximum of shear stress. If all particles are of equal strength, the rate of dispersion is independent of time, although the total change in dispersion is not. The relationship between dispersion and processing time is shown in Fig. 1

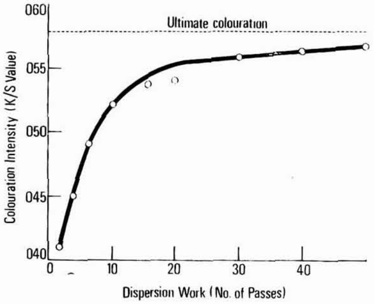

Fig. 1. CI Pigment Green 7 mixed with white base on a laboratory mill (9)

The total change in dispersion, and hence the ultimate colouration developed, is dependent upon the energy of the mixing process. As the time of mixing is increased, the value for the total change approaches, asymptotically, a maximum level corresponding to that achieved by mixing for an infinitely long time at that level of shear. But long processing times do not compensate for a lack of intensity of shear and no matter how long the process is extended, low shear levels will not generate good colour development. This relationship has been observed with many different pigments.[9, 11]

There are several ways to derive a single number that will describe the level of pigment dispersion. Pigenot[10] has obtained colour development curves by plotting colour strength against the work done during mixing. By assuming this development curve (Fig. 1) to be hyperbolic, he has been able to obtain a straight line (as shown in Fig. 2) by plotting the reciprocal values of work done against the colour strength developed.

If F is the strength of colour developed, and E the work expended, then the straight line may be represented by:

$$\frac{1}{F} = a + b.\frac{1}{E}$$

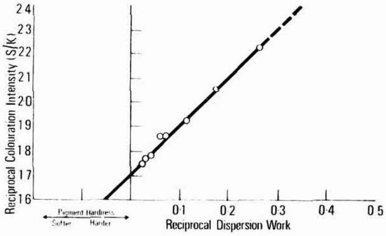

Fig. 2. Dispersion of CI Pigment Green 7 into White base deduced from Fig. 1 (9)

The hardness of the pigment particles which are so dispersed is given by the intercept on the abscissa.

However, it is difficult to justify this approach on a theoretical basis since the dispersion which occurs is dependent upon the number of dispersible particles present, and upon them being subjected to high shear levels. This means that dispersion is a first order reaction because the rupture of the agglomerate is the rate controlling step.[16] It may be expressed as

$$\frac{dN}{dt} = -RN$$

where N is the number of dispersible particles

t is time, and

R is the rate of pigment dispersion.

Rearranging this equation and integrating gives

$$\log_e N = -Rt + K$$

The number of dispersible particles is given by the area under the size distribution curve between the limits imposed by (a) the largest particle present, and (b) the smallest dispersible particle.

Dispersion becomes progressively more difficult as particle size decreases and at some threshold size ceases completely. This aspect of dispersion will be discussed in more detail later. As yet there is no means available by which the strength of these small pigment particles may be measured, and therefore no definite idea may be formed of the size of the smallest dispersible particle or of the way in which this changes with the ambient rate of shear.

Since dispersibility varies with agglomerate size, it is to be expected that each size would disperse at a different rate. The observed rate of dispersion in a population of particles containing a range of different sizes will thus be given by the average of all the individual rates of dispersion. Since the rate of dispersion for small particles is much smaller than it is for the large ones, small particles will contribute very little to the overall observed rate during the early stages of mixing. As the mixing cycle is extended, and the large particles disappear, the small particles will become more dominant and the rate of dispersion will fall. This may, or may not be noticeable, depending upon the level of shear and the difference in dispersibility between the large and small particles.

If the total number of dispersible particles were plotted on a logarithmic axis against time a straight line would be expected. However, this does not occur in practice, and deviations from linearity increase as dispersion proceeds. This results from the more serious errors associated with counting the large irregular particles of low frequency.

These errors can be practically eliminated by using the total change in population instead of the number of particles left. The errors of sampling are reduced because the number which includes them is subtracted from one which is much larger. A straight line graph can then be obtained by plotting the change in dispersion (that is, the change in the number of particles) against the logarithm of the time required to produce it. The slope of this line represents the rate of pigment dispersion.[15, 17]

Factors affecting dispersion

As might be expected, the level of dispersion achieved with any mixing process depends upon the energy required to disperse the agglomerates, and the capability of the process for supplying that energy. The two aspects of this relation may be examined separately. Indeed, some steps have already been taken along similar lines.[1, 11, 20]

The mixer used for a compounding operation will, by the nature of its design, determine the maximum level of shear which may be developed within any given polymer at any operating temperature. It is well established for example, in the paint industry, that every mill develops a specific energy, which in turn limits the level of dispersion finally achieved.[14, 20]

Design will also control the residence time (that is the time for which the agglomerates are exposed to shear) as well as the proportion of that time during which the agglomerates are exposed to high rates of shear. Time must be allowed, in any mixing process, especially in batch mixing, to ensure that all the agglomerates which are present pass through the zone of highest shear. Other variables limit the shear developed during mixing and these include the operating temperature, the nature of the polymer and the mixer speed. Higher speeds raise the energy input as well as passing material through the zone of maximum intensity more frequently. Thus more agglomerates are dispersed more quickly.

If the agglomerates are to be dispersed at all, the shear which has been developed in the polymer must be communicated to them. This will depend upon the adhesion between the polymer and the pigment, and the formation of a common interface. This is often referred to as pigment "wetting," and involves the displacement of air and the maximisation of the interface. Not all of the pigment surface will be accessible to the polymer, and the proportion of the surface actually wetted will be less than that which would be expected in liquid systems.

The size of the agglomerates is also important. For a given shear gradient, the smaller the pigment particle, the smaller the proportion of total shear to which it is exposed.

These process variables only determine the apparent strength of an agglomerate. Its real strength is determined by the physical characteristics of the material concerned, the cohesive and tensile strengths of the powder determining the level of agglomeration both before and during powder mixing. As the agglomerates become more compacted, due to handling and mixing, they develop strength and their density increases. As compaction continues the strength of the particles approaches that of the crystalline material.

It is perhaps fortunate that the strength of the agglomerate is unlikely to reach that of the constituent material in mass form. This is due to the high voids content which is to be expected in a compacted powder, as well as to the presence of cracks and strains. Griffith[21] found that deviation from the theoretical strength, introduced by flaws, and especially those at the surface, occurs at the worst flaw oriented in the direction of the applied stress. The extension and ultimate failure at this point is made possible, and indeed probable, by the concentration of the applied stress at its tip. In other words "a force must be applied to the agglomerate which is sufficient to overcome the interparticle forces, and which uses the axis of the particle as a mechanical lever through which to apply the forces".[22]

The strength of an agglomerate is thus limited to the likelihood that it contains at least one suitably oriented flaw. Small agglomerates will therefore be relatively, even intrinsically, stronger than large ones since they are less likely to contain flaws. This increase in strength with reduced size has been encountered elsewhere.[23, 25] The situation is complicated further by the momentary elastic deformation which is possible for some particles, by means of which they can pass through the high shear zone of the mixer without being dispersed.

Similar conclusions may be deduced using different criteria. McKelvey[26] has considered the dispersive mixing of polymer and agglomerates which consist of particle pairs suspended in a viscous medium. If the particle concentration is kept low to avoid interactions, the effective forces may be considered to be the cohesion within the agglomerate and the surface forces exerted by the polymer matrix upon the agglomerate. He concluded the following:

1. High shear promotes dispersion.
2. Provided that the shear is sufficiently great, and there is turbulent flow, in time each particle will encounter the dispersing force.
3. There is some threshold stress below which no dispersion will occur.
4. Only those particles which have a favourable spatial orientation will be dispersed.
5. Provided that the interaction between the particles which comprise the agglomerate is independent of its size, then the large agglomerate will disperse more easily than the small one.

Experimental

Pigment powder was tumble mixed with polyethylene granules to produce a uniform, non-segregating mixture containing 1 per cent pigment. Samples of the mixture were placed in a Brabender Plastograph[18, 19] and maintained at 140°C for ten minutes so as to allow the polymer to soften before mixing for 10 seconds and 1, 3, 7, 15 and 30 minutes. The Brabender Plastograph is a highly sophisticated laboratory version of the Banbury mixer. It has been used extensively for dispersion and stability studies in the paint industry[16] and is well suited to compounding plastics mixtures under controlled conditions.

The samples so produced were removed, compression moulded into flat plaques, sectioned with a microtome, mounted on a glass slide and evaluated with the "Quantimet." By this means it was possible to obtain an oversize cumulative frequency distribution (the number of particles greater than a series of chosen sizes) which describes the pigment dispersion being examined. The data so obtained were checked for obvious errors which, if present, were corrected before converting to a size frequency distribution. After this, a series of mathematical processes were used to correct for sampling errors, and by fitting a polynomial equation to the distribution curve, the area which it enclosed was calculated.[17]

The area so obtained, being a measure of the number of particles present between the size limits selected, can be used to show how dispersion is proceeding. If changes in area are plotted against the logarithm of the processing time,[17] a straight line is produced, the slope of which gives the rate of pigment dispersion.

There are many potential sources of error in particle size analysis (inhomogeneity, errors of sampling, sampling procedures which introduce bias, errors of measurement etc.), but if the experiments are designed to take them into account their importance may be greatly reduced.[14, 15] Having given attention to these matters, a relatively high level of repeatability is possible. It must be emphasised, however, that the "Quantimet" is not capable of measuring absolute quantities unless special time consuming checks are made using standard samples. It was effectively used in this experimental work as a means of measuring differences.

The range of pigments selected was designed to cover as many different chemical types as possible. Most of them had already been examined, when tensile strength was related to powder compaction.[27]

The pigments used were:

1. Elf 75, a medium flow channel black (*Cabot Carbon Ltd.*)
2. Black Pearls 83, a densified, granulated channel black (*Cabot Carbon Ltd.*)
3. Polymon Blue LBS, a full shade α-form copper phthalocyanine (*ICI Organics Division*)
4. Cobalt Blue 6305 (*Blythe Colours Ltd.*)
5. Blue N3756, a cobalt blue (*J. C. Baines Ltd.*)
6. Ultramarine Blue M6925 (*Reckitts Colours Ltd.*)
7. Turkey Red Oxide R27, synthetic iron oxide (*Golden Valley Colours*)
8. Polymon Green GN500 (*ICI Organics Division*)
9. ED Polymon Green GN (*ICI Organics Division*)
10. Polymon Green GS (*ICI Organics Division*)
11. Polymon Green YS (*ICI Organics Division*)
12. Chromium Oxide: W Grade (*Associated Chemicals*)
13. Cadmium Deep Yellow P543 (*Blythe Colours Ltd.*)
14. PV Fast Red E3B, a quinacridone (*Hoescht*)
15. Rubine Toner 2BS (*ICI Organics Division*)
16. Cadmium Red P436 (*Blythe Colours Ltd.*)
17. Cadmium Light Red 6785 (*Blythe Colours Ltd.*)
18. Cadmium Red SM1426 (*Metallin Co. Ltd.*)
19. PV Fast Red B, a perylene (*Hoescht*)
20. Cinquasia Violet R : RT-791-D, a quinacridone (*Du Pont*)
21. Kronos RA41 (*Kronos Titanium Ltd.*)
22. Tioxide R-SM (*Tioxide International Ltd.*)
23. Tioxide R-FC2 (*Tioxide International Ltd.*)
24. Tioxide R-TC2 (*Tioxide International Ltd.*)
25. Yellow Oxide BC (*Reckitts Colours Ltd.*)
26. Irgalite Yellow WSC (*CIBA-GEIGY*)
27. Irgalite Yellow WSR (*CIBA-GEIGY*)
28. Microlith Yellow 2GT (*CIBA-GEIGY*)
29. Chromophtal Yellow 3G (*CIBA-GEIGY*)
30. Microlith Yellow 3G T (*CIBA-GEIGY*)

Results and discussion

Reproducibility

Cobalt Blue 6305 and Cadmium Deep Yellow P543 were individually mixed with polyethylene using the Brabender Plastograph. Mixtures were produced at three different mixer speeds, 15, 30 and 60 rpm, using two different mixers, and then evaluated using two different "Quantimets." The results are shown in Table 1.

Table 1

Rate of pigment dispersion measured on different occasions

Cobalt Blue 6305	Rate of mixing (rpm)			Mixer	Quantimet
	15	30	60		
Sample 1	0.76	0.93	1.06	A	A
Sample 2	0.80	0.97	1.12	A	B
Sample 3	0.79	1.09	2.50	B	B
Cadmium Deep Yellow P543					
Sample 1	0.92	1.10	1.63	A	A
Sample 2	1.23	1.90	3.30	B	B

A comparison of these figures illustrates the degree of reproducibility achieved with samples which were prepared at different times, and evaluated at different times by different instruments and operators. The most noticeable difference in these results was in the level of dispersion achieved at high mixing speeds using different mixers, and arose from the different configuration of the blades in the two mixers. Calculations of maximum shear rate made using the measured clearance between the tips of the blades and the mixer wall, are shown in Table 2, and these explain the differences found between mixers in Table 1.

Table 2

Approximate rates of shear (sec^{-1}) for the Brabender Plastograph

Speed of Rotation (rpm)	15	30	60
Old Brabender, Mixer A	42	84	168
New Brabender, Mixer B	97	194	387

Midway through the examination of the pigments listed above, the Brabender Plastograph broke down and work had to be transferred to a new machine. Although these two mixers developed considerably different rates of shear, comparisons between different pigments evaluated on the different machines is valid, provided that it is done at equivalent rates of shear. This is demonstrated in Fig. 3 where measured rates of dispersion obtained on both Brabender Plastographs using Cobalt Blue 6305 and Cadmium Deep Yellow P543 have been related to the maximum rate of shear developed in the mixer.

Measured dispersibility

The results of these studies into rate of pigment dispersion are shown in Figs. 4 to 7, where the rate of dispersion is plotted against shear. There are several features which are immediately noticeable.

1. In general, the inorganic pigments dispersed more easily and more quickly than the organic pigments, though the difference was not sufficiently large to prevent the two groups from overlapping.

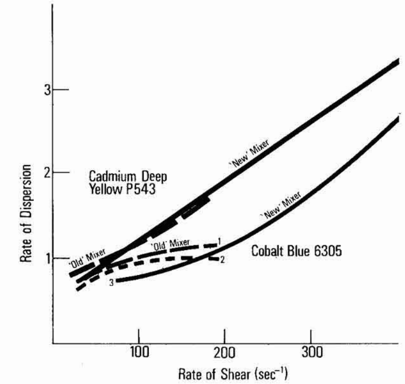

Fig. 3. The variation in dispersion with rate of shear using different mixtures

2. In nearly every case, when the rate of shear was changed, the rate of dispersion changed also. There were several distinct types of response:
   (a) where the rate of dispersion remained almost unchanged. This was only encountered once—with ED Polymon Green GN, and it is probable that since this pigment is already dispersed, the slight variation in the measured dispersion is related to the different rates of distribution involved;
   (b) where the rate of dispersion increased with increasing rate of shear. Here there were three distinct types of behaviour:
      (i) a linear response, where the rate of dispersion was proportional to the rate of shear. Examples were provided by Cadmium Red P436 and Cadmium Deep Yellow P543 in Fig. 7;
      (ii) a non-linear relationship where rate of dispersion fails to increase in proportion to the increasing shear. Examples were provided by Polymon Blue LBS and PV Fast Red E3B in Fig. 4;
      (iii) a non-linear relationship where the rate of dispersion increased much faster than the rate of shear. Examples were provided by Ultramarine Blue M6925 and Turkey Red Oxide R27 in Fig. 5;

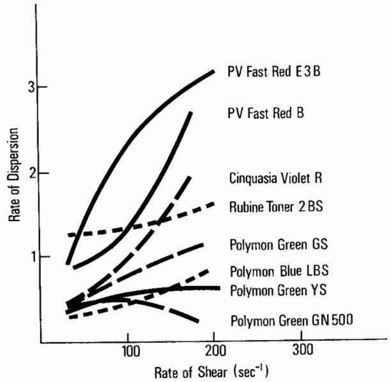

Fig. 4. Rates of dispersion for various pigments using the "old" mixer

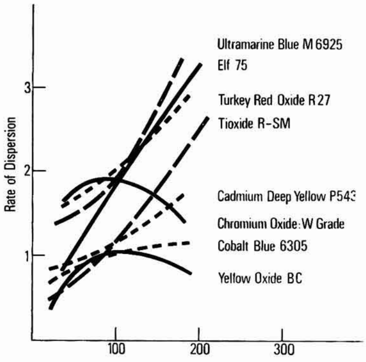

Fig. 5. Rates of dispersion for various pigments at different rates of shear, using the "old" mixer

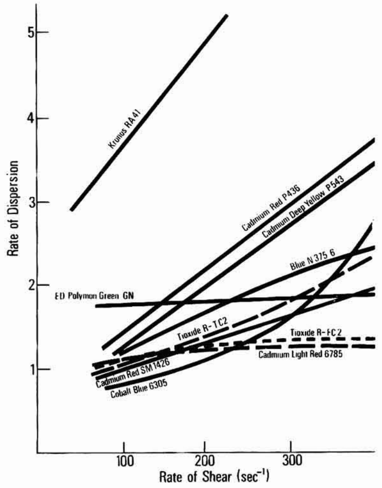

Fig. 6. Rates of dispersion for various pigments at different rates of shear using the "new" mixer

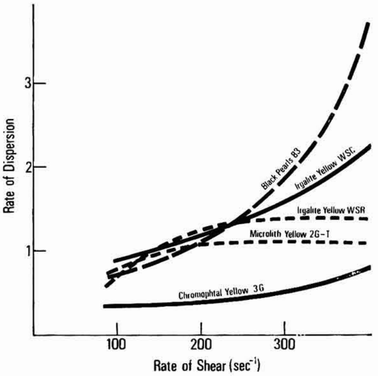

Fig. 7. Rates of dispersion for various pigments using the "new" mixer

(c) where the rate of dispersion fell off badly as shear increased, so much so that at high shear levels it was worse than at lower shear levels. Examples were provided by Polymon Green GN500, Chromium Oxide: W Grade and Yellow Oxide BC. This type of behaviour has already been reported for Polymon Green GN500 when mixed into white polyethylene[28] using a two-roll mill (where rate of shear was varied by changing nip size), and for CI Pigment Blue 56, an alkali blue sulphonic acid, when milled into a paint medium[14].

The reasons underlying these differences between the pigments are by no means clear. They can be partly explained by considering the physical properties of the pigment.

Organic pigments have a much smaller particle size than inorganic pigments. As a result the interparticle forces are of much greater importance and the powders can support a greater voids content. This enables the powder to compact much more easily, and the greater number of interparticle contacts allows greater tensile strengths to be developed in the agglomerate[27].

Changes in dispersion rate with the rate of shear may be attributed to variations in the wetting of the pigment surface by the polymer. As adhesion between the pigment surface and the polymer improves, so does dispersion. But if this adhesion falls off at high rates of shear (that is, the polymer separates from the pigment), then dispersion will less easily be accomplished. Also, since stress is applied to [illegible] agglomerate for a shorter period of time at high rates of shear, the particle may be able to deform without being fractured.

It is more difficult to explain the excessively improved dispersion rates at higher shear. They may well result from relatively inefficient dispersion at low shear rates which results in the dispersion which is obtained at high shear looking much better than it really is. This would occur if "dewetting", or stripping, required a definite time in which to occur, and agglomerates which were not subjected to shear for times as long as this would be dispersed normally.

Conclusions

The total change at any time in a dispersion (as measured by comparing particle size distribution) is dependent upon the time of mixing.

The ultimate level of dispersion achieved depends upon the maximum shear available in the mixer. The higher this rate of shear, the greater the change in dispersion.

The maximum level of dispersion is approached assymptotically as mixing proceeds. This behaviour is analogous to radioactive decay, and shows that dispersion is a first order process.

Pigments differ considerably in their response to shear; in general inorganic pigments disperse more easily than organic pigments.

The relationship between rate of dispersion and rate of shear has been found to differ also. There are several types of behaviour:

(i) where the rate of dispersion was almost independent of shear (predispersed pigments);

(ii) where dispersibility increased with rate of shear

(a) having a linear response,

(b) having a non-linear response, dispersion increasing more slowly,

(c) having a non-linear response, with dispersion increasing more rapidly;

(iii) where dispersibility actually deteriorated with increasing shear levels.

A comparison between mixtures produced on two different mixers has shown that:

(i) the method provides reasonable reproducibility,

(ii) there is good agreement between dispersibility values obtained over a wide range of shear levels.

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The effect of pigments on the penetration of sulphur dioxide into coatings

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Summary

The presence of pigments causes a decrease in the rate of penetration of sulphur dioxide through a coating to the extent of 50-70 per cent, according to the type of pigment present, in comparison with the rate of penetration through an unpigmented lacquer film. Alkyd resin films pigmented with zinc oxide, titanium dioxide or metallic lead powder and films based on chlorinated rubber pigmented with metallic lead were used in the tests.

Keywords

Properties, characteristics and conditions primarily associated with:

dried or cured films
permeability

the environment
sulphur dioxide concentration

L'influence des pigments sur le pénétration de l'anhydride sulfureux à traverse les couches de peintures

Résumé

La présence des pigments dans la peinture diminue de 50-70% la vitesse de pénétration de l'anhydride sulfureux à travers de la couche de peinture en rapport avec la sorte du pigment, et en comparaison avec sa vitesse de pénétration par le film de vernis non pigmenté. Les films de peinture à base de résine glycérophtalique pigmentés au blanc de zinc, au blanc de titane et à la poudre de plomb, et les films de peinture au caoutchouc chloré pigmentés à la poudre de plomb ont été utilisés.

Der Einfluss von Pigmenten auf das Durchdringen von Austrichfilmen durch Schwefeldioxid

Zusammenfassung

Die Anwesenheit von Pigmenten im Anstrichstoff reduziert in Abhängigkeit von der Pigmentart um 50-70% die Durchdringungsgeschwindigkeit des Schwefeldioxides durch den Anstrichstoff im Vergleich mit seiner Durchdringungsgeschwindigkeit durch den nichtpigmentierten Lackfilm. Es wurden die mit dem Zink- und Titanweiss und Pulverblei pigmentierten Alkydanstrichfilme und die mit dem Pulverblei pigmentierten Chlorkautschukanstrichfilme benützt.

Влияние пигментов на проникновение двуокиси серыв п окрытия

Резюме

Присутствие пигмента в лакокрасочной пленке понижает на 50-70% скорость проникновения двуокиси серы в сравнении со скоростью проникновения SO_2 в лаковую пленку не содержащую пигмент. Изучали алкидные лакокрасочные пленки содержащие цинковые белила, титановые белила и свинцовую пудру и пленки на основе хлоркаучука осдержащие свинцовую пудру.

Introduction

The results of a study of the penetration of sulphur dioxide into unpigmented resin films have been described in a previous paper.[1] Coatings used for the protection of mechanical equipment and steel construction always contain pigment in addition to the film-forming component. It was considered probable that the presence of pigment in a protective coating would exert some effect on the rate of penetration of sulphur dioxide through the films.

Experimental

Typical coatings based on alkyds,[1] pigmented either with zinc oxide, representing a reactive pigment, or with titanium dioxide, representing a non-reactive pigment were used in the present work. The experiments were extended to cover paints pigmented with metallic lead powder (Spelthorne Metals Ltd.) and based upon: (a) a pentaerythritol alkyd resin containing about 70 per cent fatty acids of drying oils together with lead, and cobalt naphthenates as driers. The solids content was 68 per cent and the paint was diluted for application with xylene in a ratio of 100:20. The details of the formulation, reference 398/177, are given in the appendix. (b) a chlorinated rubber paint, plasticised with a chlorinated paraffin and pigmented with metallic lead. Details of the formulation, reference 398/175, are given in the appendix. The binder consisted of a mixture of Alloprene R 20 and Cereclor 42 in the proportion of 2:1 by weight, dissolved in a mixture of xylene and tetralin (Shellsol) in the proportion 7:3 by weight. (c) the unpigmented alkyd used in the previous work,[1] for purposes of comparison.

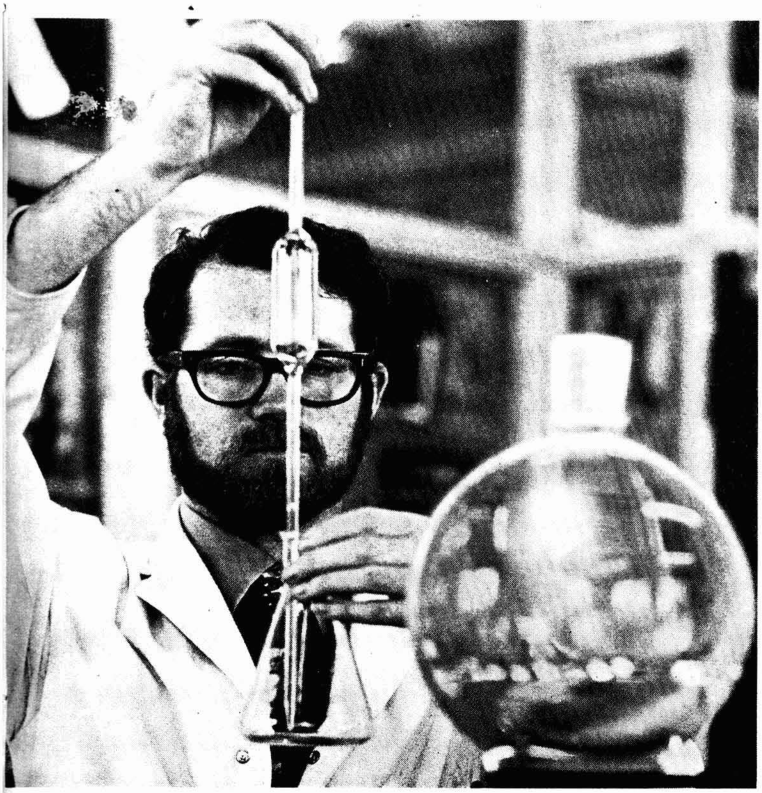
The paints containing zinc oxide and titanium dioxide were based on a 50 per cent solution of the alkyd resin used in the earlier work, and were formulated to give pigment volume contents of 5, 10, 20 and 30 per cent.

FAT-FAX 10

FAT-FAX . . . in which Price's Chemicals Ltd – Britain's largest oleochemical manufacturer – talks a bit about its raw materials, its processes, its products and their applications. FAT-FAX 10 is the second in a series of FAT-FAXes devoted entirely to SURFACE-COATING applications. Price's might prove relatively immodest when it comes to a knowledge of oleochemicals; on second thought, read 'does' for 'might', and 'thoroughly' for 'relatively'. But when it comes to oleochemical *applications*, Price's modesty is real, and fully justified. You, gentle reader, are the expert here – and we'll not forget it. Yet we dare to hope that the information in this series will prove useful, thought provoking, readable or (with luck) all three.

Frankincense speaking, myrrh's not everybody's cup of resin.

St Matthew's implication that these two secretions of *Boswellia carteri* and *Commiphora abyssinica* (respectively) were as good as gold, shows that resins have a long and honourable history. Nowadays of course natural resins have been succeeded by the much more flexible and adaptable synthetics, the alkyds, polyesters, epoxys, formaldehydes, and so on that are the basis of the modern surface-coatings industry. But natural resins – those sticky substances exuded by certain trees when their bark has been damaged – were basic raw materials of lacquers and varnishes for thousands of years, going back to the Incas, the ancient Egyptians, the Carthaginians, the Phoenicians and a lot of other old people whom one no longer sees about. There was once a queen of Cyrene, we are told, much given to the wearing of amber (a fossil resin). Her name was Berenice, whence we are led via the usual etymological degradations to *pheronice, verenice, vernis* (Old French) and eventually, *varnish*. Meanwhile, on the other side of the earth, the ancient Japanese were making lacquer by secret processes from the resin of *Rhus vernicifera*; this coating dries only in the dark, and can produce serious skin irritation not unlike poison ivy. Just two more reasons why surface-coatings people are grateful for synthetic resins (and the Price's chemicals that help make them).



Now we all appreciate polymerisation quite kienle

Making big molecules out of little ones is pretty basic to the surface-coatings business. Before 1930, however, the rules governing polymerisation were little understood, even among those paint and varnish people who'd been successfully practising it for years. Then, writing in *Industrial and Engineering Chemistry's* June issue (Vol. 22, No. 6), 34-year-old Ray Kienle (Ph.D., M.I.T. 1928) cleared up a lot of the confusion with his concept of 'functionality'. An organic molecule, said Kienle in his 'Observations as to the Formulation of Synthetic Resins' can have one or more reactive groups – such as hydroxyl, carboxyl, amino, epoxy, or unsaturation as represented by a double bond. The molecule's functionality, then, equals the number of these reactive groups it contains. Now for Dr Kienle's famous postulates:

1. In polymerisation, the reacting molecules must each have a functionality of at least 2.
2. Polymerisation takes place through *random* contact of activated reactive groups.
3. The resulting polymer's physical properties are determined by the size and shape of the reacting molecules.

Some molecules of functionality 2: glycols, amino acids, ethylene. Pentaerythritol's functionality is 4, but butadiene's is either 2 or 4, depending on whether one or both of its double bonds react. A splendid polyol of functionality 2.8 is, as it happens, Price's Glycerine – of which (much) more later.

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Films were prepared on a polyethylene support from which they were removed, by peeling, after drying. Successive coats were applied at 24 hour intervals. The structures of the free films are shown diagramatically in Figs. 1 and 3.

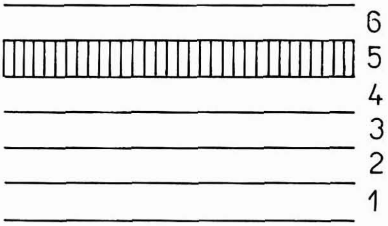

Fig. 1. A schematic representation of single layers of free film 1-4, 6—alkyd unpigmented layers

5—the pigmented layer

Fifty-seven days after the last coat of paint had been applied the films were subjected to the action of a 0.0005M solution of sulphur dioxide at 40°C. The overall test period was 46 days. Tests had to be discontinued with the films containing 30 per cent titanium dioxide because of separation into layers. It should be mentioned that breakdown also occurred with various other films. In the case of white pigments the penetration of sulphur dioxide into the film could be detected by using an indicator.

The results obtained with the white pigments are shown in Fig. 2, from which it can be seen that the presence of only 5 per cent pigment decreases the penetration rate by about 40 per cent in comparison with the unpigmented alkyd resin film. The effect of a further increase in the pigment content is less pronounced. The difference between the reactive zinc oxide pigment and the non-reactive titanium dioxide was not marked; this point needs further clarification by experiments on other pigments and acid solutions.

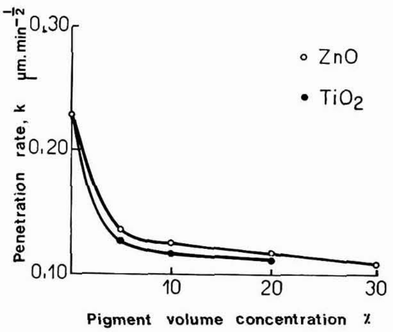

Fig. 2. The dependence of the rate of sulphur dioxide penetration on the zinc oxide and titanium oxide content in an alkyd film

In the case of paints pigmented with metallic lead, it was impossible to detect the entry of SO_2 by direct colouration of an added indicator. Penetration can be deduced only by the passage of SO_2 into the adjacent unpigmented resin layer.

The media used in the preparation of the free films are given in Table 1.

Table 1

Coating materials

Film	*Coating material*
A	Alkyd as used in ref. 1. Coating formulation 398/177
B	Alkyd. Scopolux 151/M/70. Coating formulation 398/177
C	Alloprene M20 + Cereclor 42. Coating formulation 398/175
D	Alkyd as used in ref. 1 for seven coats

The rate of penetration of sulphur dioxide from a 0.0005M sulphur dioxide solution at 30°C into the unpigmented binders used is given in Table 2.

Table 2

The rate of sulphur dioxide penetration from a 0.0005M solution into unpigmented films at 30°C

(The test period is 30 days and the tests commenced six weeks after applying the last coat of the film)

Film	*Penetration rate, k* *μm min$^{-1/2}$*
Alkyd (pentaerythritol modified with 65% linseed oil fatty acids)[1]	0.177
Scopolux 151/M/70 (pentaerythritol alkyd, modified with about 70% drying oil fatty acids)	0.185
Alloprene R20 + Cereclor 42	0.0

The slightly higher value for Scopolux 151/M/70 compared with the other alkyd is probably due to its higher fatty acid content. However, it should be noted that the difference is within the range of experimental error.

In another series of tests, carried out over a period of 317 days, the penetration of sulphur dioxide from a 0.0005M solution through the pigmented layers 2 and 5 (Fig. 3) into the unpigmented layers 3 and 4 was followed at 30°C and from the data in Table 2, the penetration rates for pigmented layers of known thickness could be calculated. The values obtained are given in Table 3.

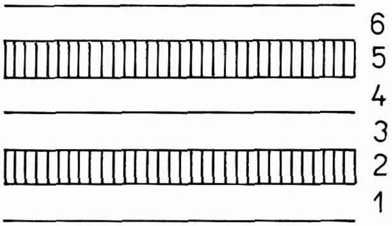

Fig. 3. A schematic representation of single layers of free film 1, 3, 4, 6—unpigmented layers of the medium identical to that contained in pigmented layers 2 and 5

Table 3

The penetration constant, k, for a paint film pigmented with metallic lead powder

Pigmented film (Description in Table 1)	*Penetration rate, k* *μm/min$^{-1/2}$*
A	0.055
B	0.066
C	0.0

Since in cases A and B the difference in composition is due to only slight differences in the alkyd resins present, an average value for k of 0.060 may be taken as the penetration rate at 30°C for this type of film from a 0.0005M sulphur dioxide solution. Comparison of this figure with those of the alkyd resins alone shows that the presence of the metallic lead pigment decreases the penetration rate by about 70 per cent, whilst the presence of zinc oxide or titanium dioxide led to a decrease of only about 50 per cent (Fig. 2).

The metallic lead pigment in the coating can catalyse SO_2 oxidation to SO_4'' ions which, as follows from the work in the earlier paper,[1] penetrate only to a small extent through the film. The lead pigment immobilises the sulphate ions as the insoluble sulphate.

Conclusion

The work that has been carried out clearly proves the importance of pigments in a film in decreasing the rate of penetration of atmospheric sulphur dioxide through to the underlying metal surface. From this point of view lead pigment is outstanding in alkyd films, which are themselves highly permeable to sulphur dioxide.

Films based on chlorinated rubber and chlorinated paraffin and pigmented with metallic lead combine the suppression of SO_2 penetration by the pigment with a film-forming medium which itself is almost impermeable to sulphur dioxide. This latter effect may be due to the size of the SO_2 molecule. Gas penetration through films of macromolecular substances depends on the gas molecule radius.[2] The SO_2 molecule's radius, derived from the second van der Waals constant, is substantially larger than that of most gases (H_2, O_2, CO_2) which penetrate relatively easily through films of macromolecular substances.

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Appendix

Composition of coatings pigmented with metallic lead

Formulation 398/175

	Per cent by weight
Rutile titanium dioxide	0.6
Barytes	18.5
Asbestine	9.2
Mica	4.6
Lead in Shellsol	22.9
Alloprene R. 20	15.8
Cereclor 42	7.9
Shellsol E	20.5
	100.0

Formulation 398/177

	Per cent by weight
Rutile titanium dioxide	0.6
Barytes	20.8
Asbestine	10.4
Mica	5.2
Lead in linseed oil	25.8
Scopolux 151/M/70	26.9
White spirit	9.4
11% Lead naphthenate	0.7
4% Cobalt naphthenate	0.2
	100.0

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The surface treatment of powdered glass fibre and stability of dispersion in polymer solution

By Y. Tamai, T. Matsunaga and K. Ishii

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Summary

Surface properties of powdered glass fibres have been measured to examine the effect of different conditions of surface treatment with a coupling agent, γ-aminopropyltriethoxysilane. The coupling conditions were: drying in a desiccator with P_2O_5 at 20°C, heat-treatment in vacuo and heat-treatment in air. The wettability by water decreased only after treatment in vacuo, whereas the stability of dispersion in a xylene solution of poly(butoxymethylmelamine) was best after treatment in air; sedimentation volume was also smallest after the latter treatment. From these results, it is considered that the silanol and amine groups of the coupling agent molecules react with and/or adsorb to the glass surface during treatment in vacuo, whilst with treatment in air only the silanol groups adhere to the glass, the amino groups being orientated towards the solution.

Keywords

Types and classes of surface
glass fibre

Resins, binders, etc.
melamine resin

Le traitement superficiel de fibre de verre pulverisé et la stabilité de sa dispersion dans les solutions polymères

Résumé

On a étudié les caractéristiques superficielles des fibres de verre pulverisés afin de déterminer l'influence qu'exercent les divers modes de traitement superficiel avec l'agent de couplage, α-aminopropyltriéthoxysilane. Les conditions de couplage étaient; séchage à 20°C dans un dessiccateur contenant de P_2O_5; traitement thermique sous vide; traitement thermique en l'air. La mouillabilité aqueuse se diminuait seulement après le traitement sous vide, tandis que la stabilité de la dispersion dans une solution de poly (butoxyméthylmélamine) en xylène était la meilleure après le traitement thermique en l'air, et également le volume de sédiment était au minimum après ce traitement-ci. En vue de ces résultats on considère que les groupements silanols et amines des molécules de l'agent de couplage réagissent avec, ou s'absorbent sur, la surface vitreuse lors du traitement sous vide, tandis que dans le cas du traitement en l'air, ce sont seulement les groupements silanols qui s'attachent à la verre, les groupements amines étant orientés vers la solution.

Die Oberflächenbehandlung Pulverisierter Glasfasern und die Stabilität von Dispersionen in Polymerlösungen

Zusammenfassung

Die Oberflächeneigenschaften von pulverisierten Glasfasern wurden gemessen um verschiedene Bedingungen bei der Oberflächenbehandlung mit einem Verkupplungsagens, dem α aminopropyltriäthoxysilan, zu untersuchen. Die Verkupplungsbedingungen waren:

> Trocknung in einem Exsikkator mit P_2O_5 bei 20°C Hitzebehandlung im Vakuum und Hitzebehandlung in der Luft.

Die Benetzbarkeit durch Wasser verringerte sich lediglich nach Behandlung im Vakuum, während sich die Stabilität der Dispersion in einer Xylollösung von Poly (Butylatmethylmelamin) nach Behandlung in der Luft als am besten erwies; auch war das anschliessende Absetzungsvolumen am kleinsten. Auf Grund dieser Ergebnisse wird angenommen, dass die Moleküle der Silanol—und Aminogruppen der Verkupplungsmittel mit der Glasoberfläche reagieren und/oder während der Behandlung im Vakuum von ihr adsorbiert werden, während bei der Behandlung in der Luft nur die Silanolgruppen am Glas haften bleiben, die Aminogruppen sich dagegen in Richtung der Lösung orientieren.

Поверхностная обработка порошкообразного стеклянного волокна и устойчивость дисперсии в полимерном растворе

Резюме

Измерялись поверхностные свойства порошкообразных стеклянных волокон для выяснения влияния различиых условий поверхностной обработки связывающим реагентом α-аминопропилтриэтоксисиланом. Условия сцепления были следующими: сушка в испарителе с P_2O_5 при 20°C, термообработка в вакууме и термообработка на воздухе. Смачиваемость водой понизилась только после обработки в вакууме-, в то время как устойчивость дисперсии в ксилоловом растворе полибутоксиметилмеламина было наилучшим после обработки в воздухе и объем осадки также был наименьшим после этой обработки. Из этих результатов авторы заключают что силаноловые и аминовые группы молекул сцепляющего средства реагируют со стеклом или адсорбируются к стеклянной поверхности во время обработки в вакууме, в то время как с обработкой в воздухе только силаноловые группы прилипают к стеклу а аминовые группы ориентируются к раствору.

Introduction

It is well known that the factors that play important roles in the dispersion stability of powders are the electric repulsion of the electrical double layer and the steric repulsion of adsorbed polymers.[1] In polymer solutions, the latter factor is believed usually to govern the stability of dispersion.[2] In this case, the method of surface treatment is considered to have significant effects on the adsorption of polymers. This is also an important factor in adhesion at inorganic/organic interfaces in composite materials, e.g., fibre-reinforced plastics.[3]

In this paper, the results of wetting by water, the stability of dispersion and the sedimentation volume of powdered glass fibres treated with a coupling agent, γ-aminopropyltriethoxysilane, that is widely used in fibre-reinforced plastics, are studied. The correlation between the above results and the coupling conditions is also discussed with reference to the adsorbed states of coupling agent molecules.

Experimental

Materials

The glass fibre, supplied by Nitto Boseki Co., is of E-glass, the diameter of which is 3μ. The coupling agent is γ-aminopropyltriethoxysilane (A-1100 from Union Carbide). The polymer, poly(butoxymethylmelamine), the molecular weight *ca.* 1100, was supplied by Nippon Paint Co. Xylene is of commercial reagent grade. Water redistilled in a Pyrex glass apparatus was used.

Preparation of powders

Before pulverising, glass fibres were washed free from the sizing agent, the main component of which is thought to be starch. After immersion for three hours in hot water at 80°C and for three hours in a hot commercial neutral detergent solution at 60°C, they were thoroughly washed by tap water, followed by rinsing in distilled water, and were dried in an air oven for 12 hours at 110°C.

The glass fibres were pulverised with an automatic agate mortar. Approximately 90 per cent of the powder fibres are in a range from 3 to 15μ in length, and the average length is *ca.* 7μ.

Surface treatment by the coupling agent

The glass powders are stirred in the aqueous solution of γ-aminopropyltriethoxysilane, followed by filtering until the water content reaches about 10 per cent. They were then dried under three different coupling conditions.

Drying at room temperature: drying in a desiccator with phosphorus pentoxide for 24 hours at 20°C (A).

Heat-treatment in vacuo: powders were heated in a vacuum apparatus under 2×10^{-2}mm Hg, for 30 minutes at 150°C (B).

Heat-treatment in air: powders were heated in the same apparatus under 1 atm of air for 60 minutes at 120°C (C).

Wettability by water

Wettability was measured by the capillary penetration method. A capillary glass tube of the inner diameter 3mm was filled with 250mg powders so that the void volume has the constant value of 40 per cent in each experiment. The lower end of the tube was immersed in water in a Petri dish and the rate of rise of the water surface in the capillary measured.

Stability of dispersion in a polymer solution

The glass powders (1gm per 10ml) were violently stirred and dispersed in a solution containing equal volumes of xylene and poly(butoxymethylmelamine), and the suspension was immediately pippeted in a graduated tube, which was then held vertically. The rate of fall of the surface of the turbid zone was measured.

Sedimentation volume

After the glass powders had been stirred and dispersed in the above solution, it was poured into a glass tube of 5mm inner diameter and the powders caused to sediment in a centrifuge. The strength of the centrifugal force was controlled by the rate of rotation and the volume of sediment was measured by the height of the sedimented layer.

Results

Wettability by water

The rate of rise of a liquid in a capillary tube of the inner radius r by capillary action can be given by[4]

$$dh/dt = (r\gamma_1 \cos\theta/4\eta h) - (r^2 d g/8\eta) \qquad \ldots\ldots(1)$$

where dh/dt is the rate of elevation, η, γ_1, d, θ and g are the viscosity, surface tension, and density of the solution, the contact angle and the gravitational constant, respectively. As the second term in equation (1) can be neglected for short times, because it must be small in comparison with the first term when η is small, then on integration,

$$h^2 = r\gamma_1 t \cos\theta / 2\eta \qquad \ldots\ldots(2)$$

Thus the slope of the lines of h^2 against t should give the relative wettability when the same liquid is used. although the exact data of r, γ_1 or η may not be known.

In Fig. 1, h^2 is plotted vs time t for the three coupling conditions as well as for untreated fibres. The powders of treatments (A) and (C) show the nearly same wettability as the untreated powders, but those treated in vacuo show the lower wettability by water. If the contact angle for untreated powders is taken to be zero, a 60 degree contact angle for treatment (B) is obtained from equation (2).

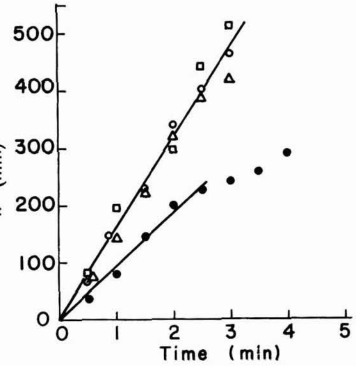

Fig. 1. Wetting of glass powders by water: ○ untreated. □ Drying at 20°C. ● Heat treatment in vacuo (B). △ Heat treatment in air (C)

From these results of wettability, it is questionable whether the powders heat-treated in the air have reacted with the coupling agent. Hence, the stability of dispersion in the polymer solution was measured.

The stability of dispersion

The fall of the surface of the turbid zone is plotted vs time in Fig. 2. The dispersion of powders heat treated in air can be said to be more stable than the three others. Since in these systems polymer adsorption may determine the dispersion stability, the results in Fig. 2 suggest that polymer has adsorbed more effectively on these powders of, in spite of good wettability by water.

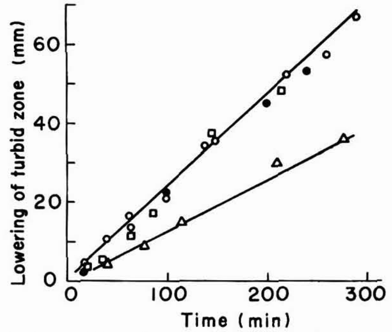

Fig. 2. The stability of dispersion of glass powders in a xylene solution containing 50 vol. % poly(butoxymethylmelamine) Key as in Fig. 1

Sedimentation volume

Fig. 3 shows the result of measurement of the sedimentation volume. For every value of the centrifugal force, the sedimentation volume shows a similar trend for different coupling conditions. Namely, the sedimentation volume decreases in order of the non-treatment > (A) $\gtrsim$ (B) > (C). This result agrees with the general knowledge that the sedimentation volume is larger when flocculation occurs easily and dispersion is unstable.[5]

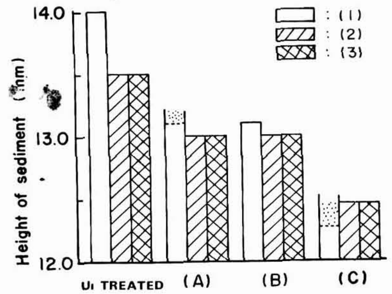

Fig. 3. Sedimentation volume from the polymer solution by a centrifugal separator: (1) 900rpm for 5 min; (2) 1,700rpm for 5 min; (3) 1,700rpm for 8 min. The dotted zone indicates incomplete sedimentation

Discussion

These results show that, even with the same coupling agent, the surface properties differ with respect to the coupling conditions and, consequently, these may be due to the different adsorbed states of the coupling agent molecules at the interface.

The powders from treatment (A) show similar behaviour to the untreated powders in terms of wettability and dispersion stability, which means that in this treatment the reaction of the coupling agent with the glass surface may not have proceeded to any great extent, and so the agent may be easily desorbed.

In treatments (B) and (C) the coupling reaction has proceeded. However, in treatment (B) the coupling agent molecules may react with and/or adsorb to the glass surface with the amino group as well as the silanol group, so that the methylene groups mainly face the outer solution and the powders show low wettability by water and low adsorption of polymers from the organic solution.

On the other hand, if the powders undergoing treatment (C) have the amino groups facing outwards, they should be wetted easily by water and could interact with melamine polymers in the organic solution.

Thus, if it is supposed that the different adsorption states are as discussed above, the results obtained in this paper can be interpreted at least qualitatively.

Acknowledgment

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[Received 11 November 1972

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Paint film thickness measurement—an X-ray fluorescent technique for thin film applications

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Summary

A new method of paint film thickness measurement, based on X-ray fluorescence techniques, is discussed. Given suitable apparatus, it is quicker, easier and more accurate than the conventional weighing methods for the type of thin films used in printing ink applications, etc. The improved accuracy is valuable in improving the overall accuracy of experimental work on opacity, where severe limitations were evident previously.

Keywords

Processes and methods primarily associated with analysis, measurement and testing

film thickness measurement
X-ray spectroscopy

La détermination de l'épaisseur des feuils de peintures—une technique, entraînant la fluorescence de rayons-X, applicable aux feuils minces

Résumé

On décrit une nouvelle méthode, basée sur la technique de la fluorescence de rayons-X, pour la détermination de l'épaisseur des feuils de peintures. Etant donné que l'appareil nécessaire soit disponible, la méthode est plus rapide, facile et précise que les méthodes classiques de gravimétrie dans le cas des feuils minces utilisés dans le domaine des encres d'imprimerie. Sa précision supérieure est d'une valeur pour l'amélioration de la précision globale des expériences sur l'opacité où de graves limitations étaient apparentes antérieurement.

Messen der Dicke von Lackfilmen
Eine Röntgenstrahlen—Fluoreszenz—Technik zur Anwendung auf Dünne Filme

Zusammenfassung

Besprechung einer neuen Methode zur Messung von Lackfilmen, beruhend auf der Röntgenstrahlen—Fluoreszenz—Technik. Geeignete Apparatur vorausgesetzt, ist sie schneller, leichter und genauer, als die konventionellen Wägemethoden, welche für die Art von dünnen Filmen für Druckfarbenauftrag etc. angewandt werden. Die grössere Genauigkeit ist für die Verbesserung der gesamten Genauigkeit experimenteller Arbeiten im Bezug auf Opazität auf einem Gebiet wertvoll, auf dem bisher starke Begrenzungen offenbar waren.

Измерение толщины красочных пленок — рентгенов ский флуоресцентный технический прием для тонких пленок

Резюме

Обсуждается новый метод измерения толщины красочной пленки, основанный на технологии рентгеновской флуоресценции. С надлежащей аппаратурой этот метод является более быстрым, более легким и более точным чем традиционные методы взвешивания для тонких пленок, применяемых с печатными красками и. т. д. Повышенная точность метода играет важную роль в усовершенствовании сумарной точности экспериментальных работ по непрозрачности, где ранее встречались существенные ограничения.

Introduction

Accurate measurements of film thickness are often required as a routine subsidiary result when tests are being conducted on paints, inks, and similar materials. This is particularly true when optical measurements are being carried out; obvious examples are the contrast ratio measurements on paints, and reflectances of roller coating finishes. Film thickness is normally measured in these cases by weighing. With Morest charts, used in contrast ratio measurements, the increase in weight of the chart after coating is used to calculate the film thickness from the known composition of the paint. Where films are prepared on some more impermeable surface, such as glass panels, the film thickness may be determined by measuring the weight loss of the panel on stripping the film. These methods give satisfactory results, when carefully carried out, for film thicknesses of about 10-15μm upwards. For thinner films, the inaccuracy of this measurement contributes a considerable proportion of the total error arising in the overall experiment, and a more accurate method is required for any work with this type of sample.

The method discussed here was developed primarily in support of research work on the optical properties of thin paint films pigmented with titanium dioxide.[1] It was quickly realised that it could be used in a variety of applications, and it has been used as a routine method for the measurement of film thickness in a wide range of systems for a number of years. Particular specific applications are the measurement of ink and roller coating film thicknesses,[2] where the improved

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accuracy over more conventional methods has proved invaluable. The test itself is more rapid than weighing methods, and although it is described here solely in terms of films pigmented with titanium dioxide, it could be adapted to materials containing other pigments.

The physical principle of this method is to determine the weight per unit area of titanium dioxide in the film using an X-ray fluorescence technique. From the known composition of the film (TiO_2 concentration) the thickness can then be calculated.

In practice a number of complications arise, both theoretical and practical. These are discussed in further detail below, but it is worth briefly enumerating them at this stage.

1. X-radiation is absorbed by the sample under test. A significant proportion of the entering exciting radiation is absorbed, as is the fluorescent X-radiation from the titanium pigment. A theoretical correction must be made for this factor.

2. It must be shown experimentally that the method is correct, and its accuracy assessed.

3. Satisfactory X-ray equipment operating conditions must be established, and standard samples prepared since the method is essentially a comparative one as the theory will show.

4. The method measures the TiO_2 content of the film and, if the paint or ink is made up by weight, the percentage of TiO_2 in the particular titanium oxide pigment under test must be known.

Theory of method

When an X-ray beam of sufficient energy falls on a sample, a proportion of the radiation is absorbed by the atoms in the sample and an electron is ejected from one of the lower lying levels in the atom. The vacancy thus formed in the electronic structure of the atom is filled by electrons coming from other levels in the atom or from the electrons originally ejected. These electronic transitions are accompanied by the emission of X-radiation, the wavelength of this emitted radiation being characteristic of the atom under consideration. This is the fluorescent X-radiation, each atom having its own spectral distribution as for visible radiation. For the purposes of this discussion the X-ray spectrometer can be treated as shown in Fig. 1. A beam of constant intensity X-radiation from the source falls at angle α on the plane sample of thickness t microns. The fluorescent radiation emitted by the sample in a direction at angle α to the surface of the sample is measured by an X-ray spectrometer which is adjusted to the wavelength of the specific radiation to be measured—in this particular case the titanium K-α emission line. The fact that the incident beam and the measured emission are at similar angles to the film is of no major physical significance, but is due primarily to the geometry of the particular measuring instrument used in this study.

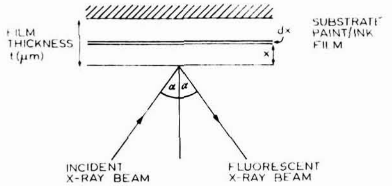

Fig. 1. Schematic diagram of X-ray beam falling on paint or ink film

The fluorescent radiation is measured by some form of detection apparatus which essentially counts the arrival of X-ray quanta of a given wavelength. The number of counts per second for a given sample depends, apart from the sample itself, on a wide range of variables, including the X-ray spectrometer design, its operating conditions and the type of radiation detector. An arbitrary "sensitivity" factor is defined for a given apparatus and set of operating conditions, as will be shown.

Neglecting absorption of the X-ray beam in the sample, all the titanium atoms are equally excited, and all the fluorescent quanta make an equal contribution to the beam reaching the detector. Since the number of titanium atoms, N, in the sample per unit area is proportional to sample thickness, t (μm), and PVC to f, then

$$N \propto f\,t$$

The signal received at the detector will be proportional to N, and in a purely conventional way it can be expressed as:

$$I = S.f.t. \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where I is the count rate at the detector in counts per second and S is the "sensitivity" factor for the equipment and operating conditions. As defined here, the units of S are counts s^{-1} (film thickness in microns)$^{-1}$ PVC^{-1}. In practice, the operating conditions of the equipment are set so as to give a maximum value of S, and hence greatest accuracy. (Typical operating conditions for the equipment used in this work are given in the Appendix.) The value of S must, of course, be determined in a subsidiary experiment—this is discussed later.

It is now necessary to correct for the absorption of both the exciting and emitted X-radiation as it traverses the specimen. This correction can be calculated theoretically by considering a thin slice of specimen, thickness dx μm, at depth x μm below the surface of the sample. This is shown schematically in Fig. 1. During its passage through the paint film, the outgoing fluorescent X-ray beam is attenuated in accordance with the normal type of absorption equation

$$I = I_0 \exp(-\mu\sigma x/\cos\alpha.10^4)$$

where μ is the mass absorption coefficient of the sample for the fluorescent X-radiation under consideration (TiKα here), σ is the density of the sample (g cm^{-3}). (The factor of 10^4 arises because the film thickness units are μm, whereas the other quantities are conventionally quoted in cm units.)

For the emitted fluorescent radiation the angle, α, is well defined by a collimation system, and the measurement is made over a narrow well-defined wavelength region. From the composition of the sample, the mass absorption coefficient for this radiation can be accurately calculated from tabulated values.

The incident beam is also attenuated in passing through the film thickness, x, in accordance with a similar equation, but here a number of complicating features arise.

The wavelength distribution of the incident beam is wide, and the absorption coefficient of the sample varies with wavelength.

The intensity distribution of the incident beam is not known as a function of wavelength.

The efficiency of the different wavelengths present in the incident beam in exciting the fluorescent radiation is not known.

The incident beam is strongly divergent and the angle α has fairly wide limits.

In order to make further progress, it must be assumed that the attenuation of the incident beam is equal to that of the emergent beam, and can be calculated in a similar manner.

The observed signal due to the slice of film thickness, dx, at depth x is therefore written as

$$dI = S.f.dx \exp(-2\mu\sigma x/\cos\alpha.10^4)$$

The factor 2 in the exponential expression allows for the double traverse of the film by the beam.

The total signal received from a film of thickness t is given by

$$I = S.f.\int_0^t \exp(-2\mu\sigma x/\cos\alpha.10^4)\,dx$$

$$I = \frac{S.f.\cos\alpha.10^4}{2\mu\sigma}\left[1 - \exp(-2\mu\sigma t/\cos\alpha.10^4\right]..(2)$$

The direct use of equation (2) to obtain film thickness on a routine test basis is impracticable, due to the form of the equation. In practice, the "apparent" thickness of the sample is calculated from equation (1).

$$t_A = I/(S.f)$$

where the pigment concentration of the film, f, is known. A correction to this value is then obtained from graphs prepared previously. From equation (2) the "apparent" thickness is given by

$$t_A = \frac{I}{S.f.} = \frac{\cos\alpha.\ 10^4}{2\mu\sigma}(1 - \exp(-2\mu\sigma t/\cos\alpha.\ 10^4))$$

In this equation, if

$$\varphi = \cos\alpha.\ 10^4/2\mu\sigma$$

then $t_A = \varphi(1 - \exp(-t/\varphi))$

Expanding the exponential gives

$$t_A = t - t^2/\varphi.2! + t^3/\varphi^2.3! - t^4/\varphi^3.4! + \ldots\ldots..$$

i.e. $t - t_A = t^2/\varphi.2! - t^3/\varphi^2.3! + t^4/\varphi^3.4! - \ldots\ldots..$

For a given set of apparatus operating conditions and type of sample, the simplest graphs to use in practice show the correction to be added to the apparent thickness. A typical working graph is shown in Fig. 2, and it will be seen that enough lines have been plotted to allow accurate interpolation. A set of these is required to cover all likely samples.

The form of the correction is plotted in Fig. 3 using logarithmic ordinates to cover the complete range of results for one type of paint. This figure was calculated for the following conditions:

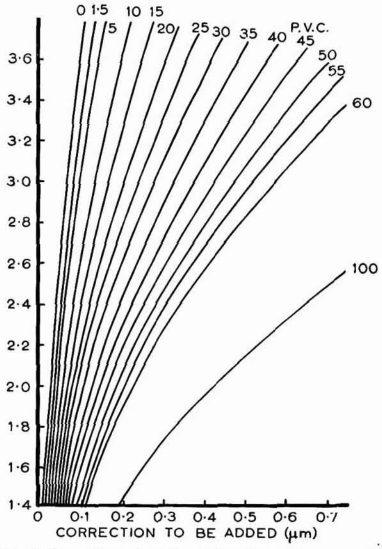

Fig. 2. Typical working chart for determining the correction due to X-ray absorption in thickness measurement

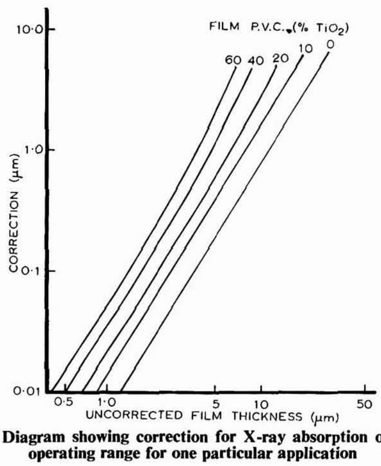

Fig. 3. Diagram showing correction for X-ray absorption over operating range for one particular application

Pigment density = 4.15 g ml^{-1}
Pigment composition = 96% TiO$_2$
Carbon/oxygen ratio in dried medium = 3:1 by weight
Density of dried medium = 1.18 g ml^{-1}
Density of thinners = 0.80 g ml^{-1}
Weight loss of thinners from medium on drying = 27.5%
Angle α = 55° (for Phillips PW1540 Spectrograph)
Mass absorption coefficient μ — Ti = 143 cm^2 g^{-1}
O = 60 cm^2 g^{-1}
C = 25 cm^2 g^{-1}

It will be noted in the above table that the percentage of TiO_2 in the pigment under test is quoted. Paints and inks are normally made up in terms of a pigment/binder ratio by weight, and the PVC calculated afterwards. The X-ray fluorescence method, however, measures only the titanium content of the film, and the PVC normally quoted must be multiplied by the proportion of TiO_2 in the titanium pigment before it is used in the formulae quoted above. When making routine tests on a given grade of titanium oxide from one manufacturer, the percentage TiO_2 will be a constant in the calculations, but if different types of pigment are being compared this correction must be taken into account. Uncoated pigments may contain over 98 per cent TiO_2, whilst modern super-refined pigments for special applications often contain less than 90 per cent TiO_2, and in the latter cases neglect of this correction will lead to an underestimate of film thickness proportional to the actual TiO_2 content of the pigment.

Experimental details

The theoretical correction for X-ray absorption in the sample which is given above is an approximation, as was emphasised in the derivation. It must now be demonstrated that this approximation is satisfactory in practice, and also that the method gives the required accuracy of measurement overall. The only realistic proof is to measure samples whose thickness has been determined accurately by an alternative means. This point of finding an alternative accurate method was the major experimental difficulty encountered in this work, since the lack of an alternative method was the precise reason for carrying out the investigation. Fortunately, there is considerable latitude here, since the method used for preparing the paint films to standardise the method need not give typical films as used in normal testing methods. The method finally adopted was to spin paint films on a very thin aluminium foil (household baking foil), cut out discs, make the X-ray measurements and then determine the paint thickness by weighing the discs before and after stripping the paint film. The practical difficulties of handling this thin metal film without creasing it were considerable and the experimental method is outlined in more detail below.

The aluminium foil used was a domestic baking foil of thickness 17.7μm. It was established that its thickness was accurately constant over wide areas and, when stretched, the surface was smooth on a microscopic scale. These factors are a necessary prerequisite to the production of an accurate, uniform paint film of constant thickness by the spinning method. A 7.6 cm diameter Tufnol disc was machined and mounted on the spindle of a paint film spinning apparatus. The foil was stretched over this disc, and held in place by using a Tufnol annular ring that was a tight push-fit over the disc when the foil was in place. The edges of the disc and ring were slightly rounded to prevent tearing of the foil. The paint films of varying thickness were spun by varying the spinning time and/or the paint viscosity. After spinning, the paint films were oven-baked to increase their rigidity before removal from the Tufnol disc. The Tufnol itself had been pre-baked before turning the disc, to prevent distortion effects. At this stage, any uneven paint films were rejected; the remainder were stored for one week before proceeding. The backs of the films were washed with methylene chloride on cotton wool swabs to remove any traces of paint that might show through the aluminium foil and affect the X-ray result.

Samples were cut from the discs to fit the particular sample holder of the available X-ray equipment. This was done with a razor blade, the sample lying on a fairly hard surface. The area of these samples was approximately 8 cm^2, and the weight of foil about 36 mg. The samples were placed in the X-ray spectrometer, and the intensity of the Ti K-α XRF radiation measured under standard conditions. The samples were weighed on a microbalance before and after removing the paint films with methylene chloride.

For the purpose of this initial trial of the method, one millbase was prepared from a commercial TiO_2 pigment and a normal air-drying alkyd. After milling, paints were prepared covering a range of PVC by diluting fractions of the millbase with varying amounts of media. The nominal PVC range produced was 2.5 per cent to 55 per cent, but the actual PVC values were accurately calculated after preparation. At certain formulations, paints were prepared at a variety of thicknesses by varying the film spinning conditions. Using the following values, available from previous work, the PVC and density of each paint was calculated from the formulation weights:

Pigment density	4.15 g ml^{-1}
Density of dry medium	1.18 g ml^{-1}
Density of white spirit	0.80 g ml^{-1}
Weight loss (of white spirit) from medium during drying	22.5%

Using the density values, the film thickness was calculated for each sample from the film weight. The sample details and the thickness determined by this method are given in Table 1.

From this value of thickness, and the X-ray fluorescence intensity results, a value for S, the "sensitivity" factor for the X-ray equipment, was calculated for each paint film. This result should, of course, be a constant, irrespective of film thickness or PVC, if the method is satisfactory. The results for each film are quoted in Table 1. The mean value of S obtained for the equipment used was $S = 998$ counts per μm per 1 per cent PVC. The experimental standard deviation of this value given by the tabulated figures is 19.2. This is not a true measure of the accuracy of thickness measurement by this X-ray technique since a variety of complicating factors arise. Also, this standard deviation includes the errors in the weighing method used to measure the thickness directly—therefore the method can only be claimed to give a standard deviation of ±2 per cent or better when used under the conditions stated here, provided that the correction for X-ray absorption in the sample is not large.

Taking the mean value of S given above, it is possible to apply the results directly and calculate film thickness. This has been attempted and the thickness results are also given in the table. The thickness measurements by X-ray method are plotted against those obtained by the weight method in Fig. 4.

Table 1

Details of sample films

Paint PVC %	Paint film weight (mg)	Paint density (g cm^{-3})	Calculated sensitivity factor (S)	Total XRF count (30 sec)	Paint film thickness from XRF (μm)	Paint film thickness from weight (μm)
56.5	3.377	2.86	968	74,830	1.43	1.49
	2.986		968	66,570	1.27	1.32
52.0	24.26	2.72	1,008	363,800	11.3	11.2
	5.868		996	124,100	2.71	2.72
	3.135		984	68,590	1.44	1.45
51.5	29.46	2.71	1,000	414,100	13.9	13.7
	5.660		1,008	122,300	2.68	2.64
46.6	17.32	2.56	984	283,300	8.34	8.52
	3.877		1,008	82,970	1.93	1.91
41.4	16.49	2.41	976	258,200	8.38	8.62
	8.495		1,016	159,900	4.50	4.44
	7.104		996	134,000	3.70	3.71
36.4	11.85	2.26	1,024	200,400	6.97	6.61
	8.107		1,040	148,300	4.71	4.53
	4.574		988	84,000	2.48	2.55
32.3	13.41	2.13	980	199,400	7.76	7.94
	5.230		1,024	91,920	3.12	3.10
	3.412		980	60,490	1.99	2.02
26.1	12.04	1.95	1,040	174,100	8.22	7.78
21.0	11.82	1.80	1,000	145,300	8.28	8.29
	5.758		1,000	68,840	4.06	4.05
15.7	7.912	1.64	992	85,320	6.03	6.08
	4.012		1,008	45,900	3.11	3.08
10.5	7.865	1.49	980	62,370	6.50	6.65
	5.755		980	46,700	4.76	4.87
5.43	4.161	1.34	1,004	20,500	3.93	3.92
5.3	5.986		1,000	28,240	5.63	5.63
2.65	5.501	1.26	984	13,760	5.41	[illegible]
Background count	—	—	—	330	—	[illegible]

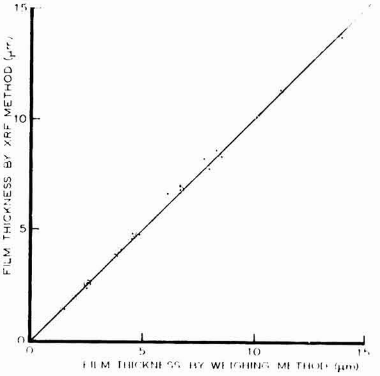

Fig. 4. Comparison of XRF method of film thickness measurement and a weighing method

The experimental results quoted above show the method to be inherently satisfactory, and to provide accurate results. In routine use, the final problem is that of determining the sensitivity factor of the experimental system. This may vary over long periods of time, and it is necessary to redetermine it every time the method is used; a procedure, of course, equivalent to a standardisation routine. Any permanent sample of known characteristics, fairly similar in nature to the experimental samples, will be satisfactory as a standard. The one used in the authors' laboratories was a paint film of 3.17 per cent PVC and 15.2μm thickness on a glass substrate.

Discussion

The experimental work outlined above was based on film thickness measurements for a particular system and using one particular X-ray fluorescence apparatus. In fact, the principles of the method can be extended to other pigmented systems. X-ray fluorescence can be used to determine the total amount of a wide range of elements, and, provided the concentration of this element in a film is known, the thickness of the film may be determined. A number of complicating factors may emerge in practice. One point to be borne in mind on all occasions is that the substrate supporting the film must be free of the element in question.

A wide variety of types of X-ray fluorescence equipment is available commercially; Whitehead and Jackson[3] have recently shown that an isotope portable analyser (Hilger and Watts) can be readily used for the determination of film thickness using the methods detailed above.

Finally, it is necessary to consider the film thickness above which the method fails to give adequate accuracy. The first point to note in this connection is that the correction to be applied for X-ray absorption at a given thickness of film increases with the PVC. If, therefore, one limits the upper thickness to be measured by quoting an upper limit to percentage correction applied for absorption, the film thickness range depends on PVC. At the present time this question has not been investigated experimentally in the authors' laboratories, but taking 50 per cent as the upper acceptable limit for the correction factor, Fig. 5 shows the upper limit of thickness measurement by this method as a function of pigment volume concentration. This figure applies specifically to the system studied experimentally in this work.

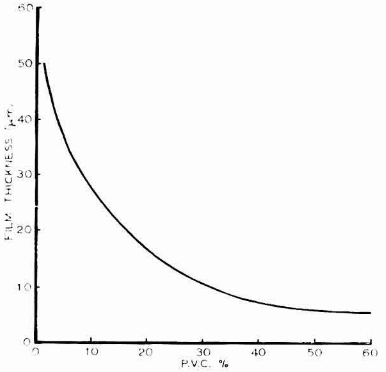

Fig. 5. Limit of application of XRF method, assuming a maximum correction of 50% due to X-ray absorption in this sample

Acknowledgment

The authors wish to thank the Directors of Tioxide International for permission to publish this paper.

[*Received 15 December 1972*

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1. Hughes, W., Murley, R. D., and Tunstall, D. F., IXe FATIPEC Congress, 1968, Kongressbuch, Sect. 1, p. 88.
2. Dowling, D. G., and Tunstall, D. F., *JOCCA*, 1971, **54,** 98.
3. Whitehead, J., and Jackson, P. T. F. Private communication.

Appendix

Details of X-ray fluorescence operating conditions

The experimental X-ray fluorescence measurements were made on a Phillips PW1540 XRF spectrograph under the following operating conditions:

X-ray tube — Tungsten, operated at 30kv, 6mA
Collimator — 150µm
Crystal analyser — LiF giving Ti Kα peak at 86.1° approximately
Crystal chamber — under vacuum
Detector — Proportional gas flow type, with pulse height discrimination
Counting Time — 30 secs

The following comments apply:

Longer counting times may be used if required.

The voltage applied to the X-ray tube must be held constant, but the current may be increased for any given set of measurements provided the thickest panel to be measured does not overload the counting circuits.

Full vacuum may be used if the dried paints are stable.

The specimen chamber must be carefully cleaned, since any powders (pigment, dust etc.) may be attracted to the paint film surface and give rise to spurious results.

Next month's issue

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

Permeability properties of surface coatings towards chloride ion *by J. D. Murray*

High-building vinyl coatings *by S. Pila*

Microbiology in the paint industry *by D. E. Hughes*

Reviews

Lackkunstharze

By Dr H. Kessler, Dr P. H. Sarx and Dr E. Schneider
5th revised edition

Munich: Carl Hanser Verlag, 1971, pp. 344. Price 85 DM.

This book, "Synthetic Resins", was originally written by Professor Wagner and first published in 1948. After his death, Dr H. F. Sarx took over from the 3rd edition. The present 5th edition has come out after an interval of 10 years, during which time a lot has happened in the ever-widening field of the subject, and the 4th edition had to be thoroughly worked over.

The arrangement of the book has remained largely as before: it consists of 11 chapters.

Chapter I is an introductory one, with definitions, conceptions and relationships.

Chapter II, headed "Polycondensation resins", is subdivided into various groups of resins, their components and variants; phenolic, amide and urea-formaldehyde resins, benzene hydrocarbon formaldehyde resins, aldehyde and ketone formaldehyde resins, polyester resins, and polyamides.

Chapter III, headed "Polyaddition resins", consists of two subsections, polyisocyanate resins (polyurethanes) and epoxide resins.

Chapter IV, "Polymerisation resins—vinyl resins", indicates the large field of vinyl polymers and co-polymers and the processes of their manufacture in almost 50 different sub-divisions.

The next six chapters are short ones. They concern polymerisation resins (indene and cumarone resins), silicone products, derivatives of the natural and synthetic caoutchouc, modified natural resins, cellulose derivatives, and miscellaneous synthetic resins. The last of these includes subsections dealing with organic polysulphide polymers, polysulphone-, polyimide-, polyspirane-resins, chlorinated polyethers and products of chlorination of multinuclear benzene derivatives.

Chapter XI, "Comments on the analysis of synthetic surface coating resins", has two main parts: preliminary tests, describing a number of specific tests, and, secondly, detection of the various groups of synthetic resins.

In an appendix one can find information about resin producers, indices for patents, authors and the subjects. The contents section is very detailed. The text includes a great number of formulae, is clearly printed and very generously annotated with about 775 footnotes on sources and references, allowing more detailed study.

Literature references reach until 1969. No resin of practical importance to the industry seems to have been omitted, though in a few places only mentioned briefly. Examples of German and foreign sources of some commercially available resins are given, together with their trade names. The reproductions of various large resin installations are interesting.

The analytical part provides a great number of "traditional" test methods, indicating sources for more detailed information. However, the importance of the more modern methods of analysis, such as those utilising one of the chromatographic, spectroscopic, and nuclear resonance methods, is also stressed.

This book has been written lucidly and with great expertise and knowledge, but concentrating on the essentials. It covers the chemical composition, production and application of synthetic resins. The many formulae reproduced should help the English reader.

In Germany, the book is considered to be one of the standard works of the surface coating industry. This new edition is again of a high level and consolidates that established position; editor and authors are to be congratulated.

M. HESS

Paint and varnish removers

By A. Williams

Noyes Data Corporation

pp. vii + 203. Price $24.00

The book is essentially a catalogue of information relating to paint and varnish removers, and is based on a study of United States patents filed between 1916 and 1972.

One hundred and eighty-one patents are quoted in detail, together with associated exemplary formulations. Removers are described under four main headings: removers based on chlorinated hydrocarbons, removers based on non-halogenated organic solvents, accelerated alkali-type removers, and acidic-type removers. In addition, there is a short section which deals with some of the lesser known and less conventional types of remover.

The presentation is very thorough, but includes much detail which might be considered unnecessary for a practical laboratory reference book. There are some obvious typographical errors (for example, "paraffin" instead of "paraffin wax"), and some of the phrasing is not precise (for example, "boiling point less than about 100°C").

The book could be a useful addition to the laboratory library, but it is not likely to add greatly to the knowledge of the experienced paint chemist, and, at 24 dollars for the limp cover edition, it seems to be priced rather highly.

C. BUTLER

Lehrbuch der Lacke und Beschichtungsmittel Band I, Teil 1 Grundlagen, Bindemittel

By H. Kittel, Stuttgart: Verlag W. A. Colomb in der H. Heenemann GmbH, 1971, pp.C + 472. Price 58 DM.

Dr Kittel is both the editor of and main contributor to this "Teaching Manual for Paints, Varnishes and Surface Coatings." There are two other major authors: Dr P. Baur, who contributes a section on historical aspects of the subject, and Dr F. M. Depke, who writes on bitumen and tar. Even in those sections of the book prepared by Dr Kittel he has been at pains to supplement his own knowledge by enlisting the services of 19 specialists to check relevant parts.

This is the first of nine planned volumes, the complete series being intended to cover the whole field of paint, with the exception of artists' colours. Dealing with polymers and binders, Part 1 contains over 200 items, starting with general history, nomenclature, and stoichiometry, and continuing with a comprehensive treatment of the chemical and physical properties of natural and synthetic resins, oils and other raw materials. A lot of the material presented will also be of use as a "refresher" for old hands in the industry. The authors are very thorough, at times perhaps too thorough, especially when the general basic facts are discussed, but the treatment is scientifically sound.

The book is described as destined for the middle echelon of paint technologists, including qualified men and, of course, as an aid for teaching. (Dr Kittel teaches at the Technikerschule für Farbe, Lack, Kunststoff in Stuttgart). The style is a little inconsistent, varying from the erudite, where considerable knowledge is presupposed, to the popular, as in the section comparing paint with mortar and ceramic mix. The subject index is at present very incomplete, although the "Register" foreseen in Volume IX may improve matters. To use the book for reference purposes, for which it is well suited, it would be necessary to scan the contents pages as well as the index.

The complete work is termed a teaching manual. If this means an aid for the teaching staff, it would be justified, but it is hard to visualise students buying and studying nine such copious volumes, particularly as the price of this first one is about £7.50. Excellent as the book in most parts is, the reviewer considers that it is too broadly based, particularly in the earlier parts, making it difficult for the reader to see the wood for the trees—perhaps a consequence of trying to do justice to so many well-meaning authoritative advisers.

Print and drawings are clearly and spaciously laid out, and the amount of up-to-date information provided is enormous, reflecting Dr Kittel's great knowledge and experience. The book is a valuable addition to the surface coatings literature.

M. HESS

Information Received

New infrared spectra of monomers and polymers from Sadtler

Sadtler Research Laboratories, Inc., of Philadelphia, has published 600 new infrared reference spectra of monomers and polymers. These two new volumes will supplement the twelve volumes of IR grating spectra which have been previously published in this collection. Included are spectra of commercially available products such as monomers, polymers, catalysts, antioxidants, modifiers and other additives which are used in polymerization processes.

The spectra have been determined on an infrared grating spectro-photometer in the 4000 to 200 cm^{-1} frequency range and are recorded on transmittance vs. linear wave-number charts. Each spectrum indicates the trade name of the product, chemical description, physical data (when available), source of sample, instrumentation and method of sample preparation.

Powder Coatings Bibliography 1972

About a year ago the Paint Research Association Library published a Powder Coatings Bibliography covering the years 1960-1971. A supplement containing over 200 references is now available covering the 1972 literature. The arrangement is similar to that of the previous edition but this time foreign language articles have been included.

Besides a patent number index, the contents lists of the 3rd International Conference on Powder Coatings, London, 1972, the 2nd North American Conference on Powder Coatings, Toronto, 1972, and Powder Coat '72, Cincinnati, 1972 are given.

Proceedings of the First International Conference on Packaging Technology

The Proceedings of the First International Conference on Packaging Technology, just published by Pira, give in one volume a comprehensive picture of important developments in packaging technology.

The conference was held at the London Hilton in March 1972 and brought together management and technologists from industries producing and using packaging in some 15 countries.

The Proceedings include all the 35 papers presented plus the discussions that followed. The price is £10 (£5 to Pira members).

Paintmakers form new marine and overseas groups

The Paintmakers Association has set up two new groups, one to deal with marine coatings and the other to handle overseas affairs.

The Marine Coatings Group will formulate Association policies on marine coatings; provide a forum for discussion of matters of common interest; foster the work of the Research Organisation at Poole; and try to promote a healthy and expanding British marine coatings industry.

Membership will be open to all members of the Association who are active in marine paints. The new group supersedes the National Marine Paint Association and the Association of Ships' Compositions Manufacturers, which have been serviced by the Paintmakers Association and will now be wound up.

The new Overseas Affairs Group has been formed to be responsible for all aspects of overseas affairs, including exports. Sub-committees will cover exports of paint from the UK, and licensing and investment overseas. The existing Export Group and European Affairs Panel will be wound up.

Microsperse PU for colouring polyurethane coated materials

International Colloids Ltd. has announced a new range of *Microsperse PU* pigment dispersions to complement their existing *PU* range. Known as the *Microsperse PU 38* series, these are based upon polyurethane elastomers and have been found particularly suitable for colouring polyurethane coated fabrics. These new dispersions are available in the same range of colours as the Series *29* but in no way supersede them.

The *Microsperse PU 29* is now widely used for colouring polyurethane finishes, for example translucent wood lacquers, protective and decorative coatings including masonry paints, floor coatings. It will be shown, together with other products in the range, at the OCCA 25 exhibition in May.

100 years of Degussa

Degussa celebrates its centenary this year; since 31 January 1873 the company now known as *Degussa* the *Deutsche Gold -und Silber-Scheideanstalt vormals Roessler* was registered as a stock company.

Thirty years before the foundation of the company the mintmaster Friedrich Ernst Roessler had come from Darmstadt to Frankfurt and had already taken a step which was to be decisive for the later *Degussa* when he took over refining activities of the Municipal Mint at the request of the Senate and the reason for the foundation of the stock company in January 1873 was to obtain further operating funds for the Roessler family enterprise, in order to be able to refine metals for the Reich coinage which replaced the currencies of the small German states.

The firm, which started operations with a capital of 1,200,000 marks has today 174 million DM stock capital and declared reserves of 253 million DM. It has 19 production units in the Federal Republic of Germany and a great number of home and foreign holdings.

Today it employs some 13,000 staff; the Degussa group some 18,500.

Berger launches new concept in multicolour spray finishes

Berger Paints, announced in February a new concept in water-based multicolour spray finishes. It will be sold in the Brolac trade range for professional decorators, ocntractors, architects and specifiers. Named *Brolac Vinyl Multicolour Finish*, it combines low-odour, low-cost, easy application and hard-wearing vinyl qualities with a carefully researched range of 16 colour combinations designed to dispel the "utilitarian" image currently associated with fleck paints.

Galloway Medal

The Institution of Corrosion Technology invites submissions for the Galloway Medal (established in memory of the late Mr J. O. Galloway, who was instrumental in establishing the Institution in 1966) which will be awarded for the first time in 1973.

The Medal will be awarded for the best essay on "Corrosion control in a specific system by practical application of electrochemical principles with an assessment of the economic gain" or project report, submitted by a candidate under 25 years of age.

New Fishburn factory at Orpington

Fishburn Printing Ink Co. Ltd. has announced the opening of a new factory situated on the Orpington Trading Estate, St. Mary Cray, Kent, which will produce both oil and liquid inks.

New Products

Dynamit Nobel extends programme

Dynamit Nobel Chemikalien have extended their programme of acid chlorides, esters, and other derivatives of aromatic dicarboxylic acids and have included terephthal dialdehyde, TDA, a genuine intermediate which can be used in the chemistry of polymers and dyes, in pharmaceutics, and in other lines.

British Titan and Union Explosives Rio Tinto (ERT) joint venture

British Titan Limited has reached agreement with Union Explosives Rio Tinto (ERT) on a joint venture to build a titanium dioxide pigment factory at Huelva, Spain. The factory will be owned and operated by a Spanish company, Titanio SA, in which ERT will hold 55 per cent of the shares and British Titan Ltd. 45 per cent.

The factory will have an initial capacity of 30,000 metric tons per annum and will use the sulphate process developed by the British Titan group. It will be located in a development zone created by the Spanish Government.

Sulphuric acid, one of the raw materials required by the new factory, will be supplied from ERT's existing plant at Huelva. The other major raw material, the titaniferous ore, ilmenite, will be supplied from the British Titan group's own sources until Spanish ore is available.

The Spanish Government has given its consent in principle to the project and, assuming that the necessary formal authorizations are also obtained, it is intended to start construction before the end of 1973.

Matting agent TK 900

The Pigments Division of Degussa, Frankfurt am Main, has recently marketed a new matting agent under the designation *TK 900*. The product is a further development of the *TK 800* matting agent which has been in use in the lacquers industry for over ten years. Degussa has succeeded in reducing the coarse component present in *TK 800* to a minimum by improving process technology. The new matting agent *TK 900* is therefore very much finer; the limit values of secondary particle size are 2 and 15 μm: the mean value is 8 μm. As the particle fineness of the product allows it to be dispersed with the dissolver, its processing costs are in many cases lower than those of the matting agent *TK 800*.

Like *TK 800*, the new matting agent *TK 900* is highly transparent, has low drying losses and good "sheen values." Degussa particularly recommends its use for matting transparent polyester lacquers, one and two-component polyurethane lacquers, air-drying alkyd resin lacquers, epoxy resin systems and artificial leather finishing lacquers.

Zeroky primers and coatings

A new generic class of very low temperature curing industrial and marine coatings has been announced by Porter Paint Company, Louisville, Kentucky, USA.

Known as *Zeroky* primers and coatings, they cure at very low temperatures, approaching minus fifteen degrees C. They may be applied by airless or air spray application equipment up to 200 microns thick in one coat. The cured *Zeroky* film is tough, elastic, and can be recoated after extensive weathering.

Rohm and Haas Primal MV-1 acrylic emulsion

Information has been received on the performance of *Primal MV-1*, the water-based anti-corrosion emulsion developed exclusively by *Rohm and Haas* in paint systems which have proved to be totally impervious to a three-year onslaught by an atmosphere saturated with sulphur and other noxious chemicals at Houston, Texas.

Primal MV-1 has been applied in several instances where the destructive environment of the Houston Ship Channel area has frequently caused expensive maintenance problems to local industry. Its most notable success has been in the protection of river tugs where the water pollution increases the maintenance headache.

Conferences, courses, symposia

Colour chemistry

The Department of Chemistry at the Paisley College of Technology has informed us that it is now running a day-release course in Colour Chemistry for Licentiateship of the Royal Institute of Chemistry (LRIC).

This is a two-year post-HNC course but the curriculum each session is, at the moment, only being offered on alternate years so that a student can start in either year, thus effectively doubling up the numbers. Details of the scheme can be obtained from Mr J. S. McLean, BSc, FRIC, Head of Department, Department of Chemistry, Paisley College of Technology, High Street, Paisley, Renfrewshire PA1 2BE.

Ordinary Members are reminded that the LRIC is one of the qualifications listed for those Ordinary Members wishing to make application for admission to the Licentiateship Grade of the Professional Grade for Ordinary Members of the Association; see regulation A.3(b) on page 71 of the January issue.

The Inter-Society Color Council

The 42nd annual meeting of the Intee-Society Color Council will be held at thr Statler-Hilton Hotel, New York, on Monday and Tuesday, 30 April and 1 May 1973. The meeting will feature a symposium on "1973 Professional Education in Color for Art and Technology." Nine short papers will be presented in late morning and afternoon sessions on Tuesday 1 May on topics describing the breadth of educational aspect of colour, and education in colour science, colour in applied art, and applied colour science. Printed abstracts of these papers, and the text of others to be read by title only, will be available at the meeting. For further information please contact F. W. Billmeyer, Department of Chemistry, Rensselaer Polytechnic Institute, Troy New York 12181.

AFTPV Congress

The tenth national Congress of the Association Francaise des Techniciens des Penitures et Vernis, Encres d'inprimerie, Colles et Adhesifs will be held from 23 to 26 October 1973. It will be organised by the Normandy Section and will take place in the new conference hall of the Parc des Expositions at Rouen. The Secretary of the Congress is M. Francis Castel, 51 cours Clemenceau, 76100 Rouen.

One year course for Licentiateship

The Polytechnic of the South Bank currently offers a one-year part-time course leading to the Licentiateship of the Royal Institute of Chemistry in Surface Coatings Technology. Arrangements have been made in conjunction with this course to enable students to satisfy the requirements for the Licentiateship grade of the Oil and Colour Chemists' Association. Further details may be obtained from Mr R. J. Ceresa, BSc, FTSC, FRIC, FIRI, FPI, Department of Chemistry and Polymer Technology.

Hull

Is the paint industry on the move?

The first technical meeting of the new year was held at the Queens Hotel, Hull, on Monday 8 January under the chairmanship of Mr F. D. Robinson. A lecture was given by Mr D. E. Eddowes, of Polymers, Paint & Colour Journal and Chairman of the London section, about the future technical changes likely in industrial finishing, the structure of the British paint industry at home and abroad, and the acquisition of paint interests by large chemical companies.

His talk, supplemented with slides, presented a great deal of interesting information about the British paint industry, including its performance relative to other European countries and to Japan and America, so giving the audience a "bird's eye" view of its industry. The entry of Britain into the Common Market would boost the sales of industrial finishes in this country and would lead to further mergers and licensing agreements. Transportation of paint across the Channel and the North Sea would not be an important consequence of reducing trade tariffs in the years ahead.

After a discussion period Mr G. R. Siddle thanked the speaker for a thought-provoking lecture. The meeting comprised twenty Members and two visitors.

J.A.H.

Newcastle

Business planning: only a numbers game?

The January meeting was held on Thursday 4 January, when a lecture entitled "Business planning: only a numbers game?" was given by Mr J. A. Willey of Berger Paints Ltd. Although the title took the form of a question, Mr Willey was undoubtedly an advocate of business planning as an essential part of any company's activities. He expressed his philosophy as the simple needs of communication within a company, the formulation of action plans and an attempt to control the future position of the company in advance.

A Planning Officer was needed to act as collator for the plan, but it was important that he should also act as a catalyst and stimulator to encourage thinking (logical, speculative, illogical and lateral).

A short management film on the uses and benefits of business planning was then shown.

Mr Willey was adamant that business planning need not be a tide of numbers. Information was supposed to inform and not confuse. It should answer the question "Where are we going?", and lay down objectives for the board of directors. It should present realistic aims which require the involvement of all sections of the company and, most important, which must be believed to be realistic.

Planning was not a finance department responsibility; although the plan must be presented in money terms, it is only a service.

This was an extremely well delivered lecture. To a subject that could have been as dry as dust Mr Willey injected his own personality and more than a little humour. The audience of 50 kept the questions flowing for what was the longest session for many years. The meeting closed with a vote of thanks from the Chairman, Mr A. A. Duel, and a rousing applause from the audience.

F.H.

Accelerated testing of durable coatings

The December meeting was attended by 34 Members who heard a lecture given by Mr E. Oakley of Tioxide International on "Accelerated testing of durable coatings". This paper had been presented previously to the Trent Valley Branch and was a late programme rearrangement.

The experimental variations covered: chloride + sulphate process titanium; five acrylic resins of differing monomer composition; various pigment binder ratios; three exterior locations—Carlton, Florida and Emmaqua; two accelerated testing methods.

Mr Oakley stated that the interpretation of the results was extremely complex, and the Spearman-Rank correlation analysis method and a computer were used.

The lecture was well received by the audience, and the speaker was subjected to a barrage of questions which were well answered. The meeting closed with a vote of thanks from the Chairman, Mr A. A. Duell.

F.H.

Scottish

The first meeting of the 1972-73 session was held at 6.30 p.m. on Thursday 12 October at St. Enoch Hotel, Glasgow. The meeting took the form of a "face to face" interview between the former Section Chairman, Mr J. Miller, and the present Section Vice Chairman, Mr A. McLean. The reason was to endeavour to find Mr Miller's opinions of a "Lifetime in the chemical industry". This form of paper, being unusual in its concept, proved to be extremely interesting, entertaining and humorous, and it provided those present, particularly the younger Members, with an insight into the problems which Mr Miller had experienced over the years. After the formal interrogation, Mr Miller agreed to answer general questions from the audience. After the votes of thanks, a presentation was made to mark the service which Mr Miller had rendered to OCCA, and the Scottish Section in particular, over many years.

The November meeting was held on Thursday 9 November 1972 at St. Enoch Hotel, Glasgow. Mr Peter Raymond of CIBA-GEIGY Ltd. delivered a paper on "Trends in organic pigments with particular reference to the printing industry". He outlined the various printing processes, making general reference to the basic raw materials used, together with formulations, then elaborated on the trends current and future, with particular reference to the role of the organic pigment in these processes. The questions which followed showed that the audience had found the talk interesting, particularly members of the Printing Management Group who had attended the meeting at the invitation of the Chairman.

H.A.M.

Thames Valley

Some recent aspects of anti-corrosive pigments

The fourth technical meeting of the 1972-73 session was held at the Beech Tree Hotel, Beaconsfield, on Thursday 25 January 1973, with Mr Tatton in the chair. Mr Sampson, of Imperial Smelting Corporation (Alloys) Ltd., gave a talk on "Some recent aspects of anti-corrosive pigments".

The annual cost of corrosion in the UK had been estimated by a government sponsored committee as £1,365 million, and it had been estimated that, by an improvement in the defences against corrosive influence using known techniques, as much as £310 million of this could be saved. Experience had shown that one effective method of combating corrosion was the use of a priming coat, preferably containing an anti-corrosive pigment, after an adequate surface preparation. The widely accepted view was that corrosion was an electrochemical process in which atmospheric oxygen and water play a part, and therefore, to function, the anti-corrosive pigment must interrupt the electrochemical cycle. Thus chromate pigments were regarded as inhibiting corrosion by the formation of stable ferric oxides at anodic sites, whilst red lead was thought to provide anti-corrosive properties by the formation of lead soaps.

Mr Sampson considered the desirable "paint" properties of a primer to be freedom from toxicity, quick drying, tolerance towards imperfectly prepared substrates, easy application, good storage stability, and compatibility with successive coats.

Many primers that had been in fashion in the past did not fulfil all of these requirements. For example, red lead primers were objectionable on the grounds of their toxicity and slow drying rate; calcium plumbate was toxic and needed a high standard of surface preparation for best results; zinc chromate was currently under suspicion because of its toxicity and failure to cope adequately with rusty surfaces.

Consideration of most of the salient features mentioned above was mandatory in modern finishing practice. Mr Sampson described how well zinc phosphate pigment in a vinyl alkyd medium fitted the qualities noted. This material was now specified by British Rail because of its freedom from toxicity and because, followed by a micaceous iron oxide paint, it gave good service. He produced a number of colour slides to illustrate the point of good protection of British Rail equipment.

Another significant stage in the development of anti-corrosive systems was the "shop primer". This concept was first described by Zansveld and Wilson in the 1950s. Previously, mill scale was removed by the slow process of natural weathering and by traditional red lead in oil priming; these have been replaced by blast cleaning and coating with anti-corrosive primer. Shipyards adopted the technique extensively after the introduction of zinc-rich primers, and the method had generally been considered very effective for combating corrosion. However, during flame cutting and welding operations, hazardous zinc oxide vapour was evolved and, whilst much effort had been expended to allay fears, red oxide primers have tended to return, in spite of their recognised inferiority.

The speaker then described some of the manufacturing aspects of anti-corrosive primers and ended with the predictions first, that the use of high build primers and top coats would continue to increase, and second, that water thinned primers containing non-toxic anti-corrosive pigments would become widely acceptable.

Possible explanations for the good behaviour of zinc phosphate were made during a question period, and the important role of the binder was noted. The vote of thanks was proposed by Mr Bishop, a member of the Thames Valley committee.

R.E.G.

West Riding

Wood, our oldest friend

A meeting was held on Tuesday 12 December 1972 at the Griffin Hotel, Leeds. The traditional Chairman's Lecture was presented by Mrs K. Driver who chose the title "Wood, our oldest friend".

Mrs Driver outlined the wide range of uses to which wood is put and the by-products which are obtained from it, and gave a detailed account of the growth of trees and the structure of wood. The timber used in house construction was generally softwood, whilst hardwood was generally used in furniture manufacture. The terms softwood and hardwood were misnomers in that they refer to timber obtained from coniferous and broadleaved trees respectively rather than the wood's physical nature.

Air and kiln drying techniques had been developed to control the rate of drying to obtain properly seasoned wood. Both hard and soft woods contain about 22-30 per cent moisture when freshly cut and this needs to be reduced to a level consistent with the application for which the timber is intended: about 11 per cent for use in a centrally heated house to 20 per cent for outside use such as fencing or gates.

Expansion and contraction must be allowed for in the design of wooden articles. For example, a large ballroom floor can move several inches over a period of time.

Mrs Driver briefly mentioned the subject of timber preservation and a discussion developed on this subject with the expert assistance of Mr J. Nicholson and Mr R. Powell of Hicksons Timber Impregnation (GB) Ltd. Mr Nicholson outlined the types of preservative in common use. The heavy oil type, such as creosote or pentachlorphenol dissolved in fuel oil, was used for protection from weathering of, for example, telegraph poles. Water-borne preservatives which are copper, chromium, arsenic complexes and finally the light oil-borne products containing pentachlorphenol or copper and zinc naphthenates were used for remedial work.

The effectiveness of treatment depended upon the degree of penetration. Whilst brush application gave a maximum of 2mm penetration, even total immersion provided only 2-3mm. Far better penetration was achieved with water-borne preservatives applied to the timber in a vacuum chamber. Release of the vacuum, followed in some cases by the application of pressure, forced the preservative into the timber.

Mr L. Silver proposed a vote of thanks for the interesting and well prepared lecture which was enjoyed by all present.

R.A.C.

A batch type paint mixing machine (the Polymill)

At a meeting on Tuesday 9 January 1973 at the Griffin Hotel, Leeds, Mr D. W. Wilkinson, Chief Development Engineer of August's Ltd., spoke on "The Polymill".

Mr Wilkinson started his talk by tracing the development of machinery for making paint from a pestle and mortar and grinding stones to the modern machines, triple roll mills, double and single roll mills, ball mills, sand grinders, perl mills, attritors and dispersers. Each machine was suitable for a particular type of paint, or met the needs of a given type of production and plant layout.

The roll mills required a premixed material and were slow in output. Sand grinders and perl mills were suitable for continuous production but required premixed material. The cavitation mixer or disperser was suitable for easily dispersed pigments and for paint thinning.

The Polymill was a machine which combined in one unit cavitation dispersion and bead milling for the batch production of paint. The machine consisted of a bowl containing grinding media and a dispersion unit. It was not necessary to premix the material before charging to the bowl and any type of pigment could be handled in a wide range of media. Dispersion was achieved due to the shear produced by the cascading action of a bead charge. Cleaning was effected using a mixture of medium and solvent from the remainder of the formulation, agitating the beads and discharging. This discharged material was the normal thinning down agent for the paint.

Answering a question, Mr Wilkinson said that a range of ballotini size is not necessary for paint production. However, for the production of printing inks a mixture of small and large had been found preferable, and in practice a mixture of sizes are produced by wear.

Depending on formulation, operating times were about 10-20 minutes for charging, 10-90 minutes for mixing, 5 minutes for discharge and 10 minutes for washing. If switching to a contrasting colour, about 30 minutes would be required for cleaning.

Sand could not be recommended as this would clog the sieve.

The formulation was critical in order to achieve optimum results, although it was always possible to achieve some sort of product. With some types of equipment the formulation needed to be correct to obtain any sort of product.

Production of offset litho ink was not practical. Due to its high viscosity, the ink could not be discharged from the machine although mixing was satisfactory. It was a requirement for effective operation of the machine that the material should be in a flowable condition.

There were a considerable number of questions asked, and Dr K. Hargreaves referred to the interest shown whilst proposing a vote of thanks.

R.A.C.

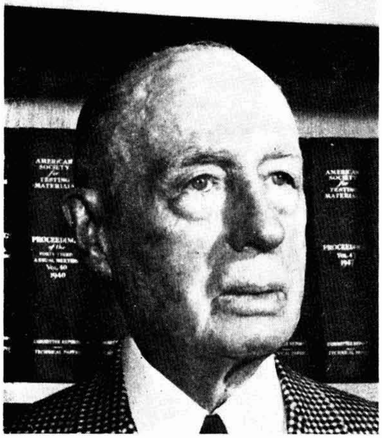
Obituary

Dr Henry A. Gardner, an Honorary Member of the Association, died on Saturday 27 January, at his home in Chevy Chase, Maryland, USA, at the age of 90.

Dr Gardner was born in Pawtucket, Rhode Island, graduated from Brown University in 1902 and also attended the University of Pennsylvania in 1903. He received a Doctor of Science degree from Lehigh University in 1928.

For many years he was Director of the Scientific Section of the National Paint, Varnish and Lacquer Association, from which he retired in 1945. He was also President and Director of the Institute of Paint and Varnish Research, Washington, DC; and held many other committee appointments in the scientific field.

Dr Gardner was author or co-author of many papers and books on paints, varnishes, lacquers and related materials, including 12 editions of "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors."



Dr Henry A. Gardner

OCCA Biennial Conference

towards 2000

eastbourne 19-23 june 1973

The total of applications received for the Association's Conference to be held at the Grand Hotel, Eastbourne, Sussex, England, from 19 to 23 June 1973 at the stated closing date for registration (31 March) included many from overseas, who will be welcomed at the customary Overseas Visitors' Reception on the opening evening. It is still possible to accept applications, but those applying from places of residence within the United Kingdom must add Value Added Tax at the standard rate to their remittances. Council has arranged a larger number of technical papers than at any previous Conference since the war in four technical and one techno-commercial session, together with three Workshop sessions. Full details of the papers were given in the December 1972 issue of the *Journal*, and biographies of the lecturers appeared in the January issue.

Registration fees

The Council has fixed the registration fees for the Eastbourne Conference at £30 for Members, £10 for Wives, and £50 for non-Members. Registered Students of the Association and Retired Members are allowed to register at 50 per cent of the Member's rate. Members attached to the London and Thames Valley Section may, if they so wish, register for daily attendance at £12 per day.

Preprints

Preprints of the papers are now being prepared, and it is expected that these, together with details of accommodation, badges, programmes, etc., will be sent to those who have registered in May. It is a feature of the Association's Conferences that preprints are sent well in advance of the function, in order to enable delegates to read them before the conference, at which the lecturers illustrate their topics but do not read the papers in their entirety. This allows for a much longer discussion period than at many other conferences, and has proved of immense value to those attending previous Association Conferences.

Dates and times of sessions

The Conference assembles on the evening of Tuesday 19 June when a reception for all those attending from overseas will be followed by a meeting of the lecturers and the chairmen of sessions. The Conference sessions will be held on Wednesday and Thursday 20-21 June, morning (9.30-12.30) and afternoon (2.30-4.30), and the morning of Friday 22 June (9.30-12.30). The Association's Annual General Meeting will take place at 2.15 p.m. on the afternoon of Friday 22 June, and this will be followed by the three Workshop Sessions. The subjects this year: "Sales forecasting", "The changing influence of the do-it-yourself market", and "The measurement of research output". The number attending each Workshop Session is strictly limited and places will be allocated in order of receipt. Where the total places for a session have been filled, later applicants will be informed and, if possible, offered an alternative session.

Receptions and dinner

There will be an informal reception for all delegates at lunchtime on Wednesday and a Civic Reception will be held, at which delegates will be welcomed by the Mayor and Mayoress of Eastbourne, on the evening of the same day. The Association's Dinner and Dance will be the closing function of the Conference on the Friday evening. Other social activities, such as coach tours, are being arranged for the benefit of ladies attending the conference.

25th Technical Exhibition

21-24 May 1973

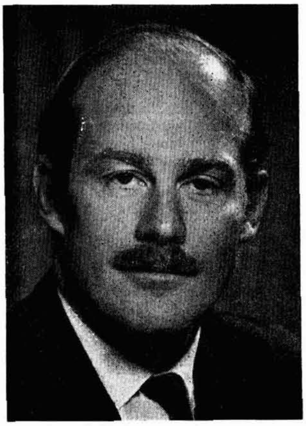
Empire Hall, Olympia, London

Over 100 stands

The Exhibition Committee is pleased to announce that it has now allocated over 100 stands with direct participation from the following overseas countries: Australia, Belgium, Finland, France, Germany, Italy, Netherlands, Norway, Sweden, Switzerland and USA.

Besides direct participation there are many companies from the United Kingdom with overseas connections so that this exhibition (the first since the United Kingdom became a full member of the European Economic Community) will be as international in its scope as many of the previous ones, which have annually attracted visitors from nearly 40 overseas countries.

Lord Limerick to be the Guest of Honour at the Exhibition Dinner



Lord Limerick

Exhibition Dinner

The Exhibition Committee is pleased to announce that Lord Limerick, Parliamentary Under-Secretary of State for Trade to the Department of Trade and Industry, has accepted its invitation to be the Guest of Honour at the Exhibition Dinner on 21 May at the Savoy Hotel and to reply to the Address of Welcome by the President of the Association, Mr A. W. Blenkinsop.

Application forms for tickets for the Dinner may be obtained from the Association's offices.

SILVER JUBILEE OCCA 25 OLYMPIA·LONDON·MAY·1973

Aims of the Exhibition

The Exhibition Committee feels that it may be worth reiterating the aims of the Exhibition as laid out in the General Rules for Exhibitors.

The aim of the Exhibition is the presentation of technical advances in those industries supplying the paint, varnish, printing ink, colour, linoleum and other allied industries. The technical advances may relate to: new products, new knowledge relating to existing products and their uses, or in suitable cases, existing knowledge which is not generally available in the consuming industries.

The Committee stipulates that exhibitors present a technical theme—that is, display in a technical manner the technical developments in raw materials, plant or apparatus illustrated by experimental evidence. It is essential that a technically or scientifically trained person, who has full knowledge of the products displayed, be available on the stand throughout the official hours of opening.

Whilst the Committee naturally encourages the showing of new products, it does not stipulate that a new product has to be shown each year, since it fully appreciates that there are occasions when this is not possible. Accordingly, the Committee draws attention to the fact that new technical data on existing products are regarded as acceptable subject matter.

Official Guide

The printing of the *Official Guide* has now been completed and copies are being circulated to all members of the Association and to chemists and technologists throughout Western Europe and to any intending visitors who have returned to the Association the cards in six languages inserted in the journals of some other societies.

Each copy of the *Official Guide* will contain a visitor's admission card, the reverse side of which must be completed before the card is handed in at the entrance to the Hall. Admission is free and each visitor will be given a folder for technical literature at the entrance.

Hours of opening

The Exhibition will be open at the Empire Hall, Olympia, London, on the following days:

Monday 21 May	12 noon-6.00 p.m.
Tuesday 22 May	9.30 a.m.-6.00 p.m.
Wednesday 23 May	9.30 a.m.-6.00 p.m.
Thursday 24 May	9.30 a.m.-6.00 p.m.

Copies of the *Official Guide* are obtainable without charge on application to the Association's offices.

Newcastle Section

Joint symposium on protective paints

The Newcastle Section, in conjunction with the North Eastern Branch of the Institute of Corrosion Technology and the Corrosion and Protection Association, is to organise a one-day symposium on protective paints at the Newcastle upon Tyne Polytechnic on 3 July. Full details will be given when available; in the interim, those interested should contact Dr K. N. Strafford, Newcastle-upon-Tyne Polytechnic, Department of Materials Science, Ellison Building, Ellison Place, Newcastle upon Tyne, NE1 8ST.

West Riding Section

Annual Dinner and Dance

The Annual Dinner and Dance was held on Friday 24 November 1972 at the Crown Hotel, Harrogate.

Mrs K. Driver (Chairman of the Section) welcomed the President and his wife, Mr and Mrs A. W. Blenkinsop, Mr A. A. Duell (Chairman of Newcastle Section) and Mrs Duell, Mr F. D. Robinson (Chairman of Hull Section) and Mr H. J. Griffiths (Immediate Past Chairman of the Midlands Section) and Mrs Griffiths.

A particularly warm welcome was extended to Mr and Mrs B. Dineen. Mr Dineen, the Business Editor of the *Yorkshire Post*, had stepped in at very short notice to act as Guest Speaker. Despite the short notice, Mr Dineen gave a very entertaining speech in which, during the more serious passages, he made particular reference to our imminent entry into the EEC and the opportunities which this presented.

Following dinner everyone adjourned to the ballroom and dancing continued until 1 a.m. The record number present testified to the popularity of this event and all were agreed that this year's function had succeeded in maintaining the high degree of success of this Yorkshire occasion.

R A.C

News of Members

Mr F. G. Dunkley, an Ordinary Member attached to the Midland Section, former Chairman of the Trent Valley Branch, Fellow in the Professional Grade and the collator of Part V of the Paint Technology Manuals, has been appointed to the board of BIE (Anti-Corrosion) Ltd.

Register of Members

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

Ordinary Members

AMONKAR, SUDHIR DINKAR, BSc, 32 Vinod Villa, Worli Estate, Worli, Bombay, India. (*General Overseas*)

CHALMERS, JOHN RITCHIE, Berger Jenson & Nicholson, Group Research Laboratory, PO Box 45, Stratford, London, E15 2DP. (*London*)

HAWARD, ANDREW MARTIN, 4 Birch Grove, Holcombe Brook, Ramsbottom, Bury, Lancashire. (*Manchester*)

HICKSON, ANTONY ROGER, Shell Chemicals UK Ltd., Resins, Urethanes and Elastomers Division, 51/55 Strand, London, WC2N 5PR. (*London*)

McDONALD, IAN MALCOLM, 252 Mortlake Road, Ilford, IG1 2TE. (*London*)

O'BRIEN, PETER WILLIAM, 27 Poplar Road, Healing, Nr. Grimsby, Lincolnshire. (*Hull*)

SHERWOOD, ALAN FRANK, 27 Falcon Road, Hampton, Middlesex. (*London*)

SIMS, JOHN LEWIS, 178 Eastcombe Avenue, Charlton, London, SE7 7LG. (*London*)

STANFIELD, RONALD JOHN, 53 Mashiters Walk, Romford, Essex. (*London*)

Associate Members

ANDERSON, PAUL RICHARD, Wych Elm, Speldhurst, Kent. (*London*)

BLACKBOND, JOHN, "Autumn Mist," Princess Margaret Road, East Tilbury, Essex, RM18 8PB. (*London*)

McKENDRICK, ALEXANDER, 4 Dudley Avenue, Edinburgh, EN6 4PN. (*Scottish*)

Student Members

CLARKSON, ANTONY RAYMOND, 9 Rokesby Park, Anlaby Park Road, Hull. (*Hull*)

MUIR, PAUL MURRAY, 29 Pendicle Road, Bearsden, Glasgow. (*Scottish*)

NEWMAN, ANTHONY LESLIE, 6 Beaufort Road, Kingston-upon-Thames, Surrey, KT1 2TQ. (*London*)

RUSH, ADRIAN SAMUEL, Hope Cottage, 351 North Road, Yate, Bristol. (*Bristol*)

Forthcoming Events

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

Monday 2 April

Hull Section: "The control of polymer lifetime under environmental condition" by Professor G. Scott. To be held at the E. H. Bullock Lecture Theatre, Hull College of Technology at 7.00 p.m.

Wednesday 4 April-Thursday 5 April

London Section: Joint Symposium with the Institute of Metal Finishing, Organic Finishing Group. "Automotive and other industrial finishing—what is the future?" to be held at the University of Warwick, Coventry.

Thursday 5 April

Midlands Section—Trent Valley Branch: AGM, followed by "Steel in fashion" by Mrs Colleran of the British Steel Corp., to be held at the British Rail School of Transport, London Road, Derby, at 7.00 p.m.

Friday 6 April

Bristol Section: Annual Dinner Dance, to be held at the Mayfair Suite, Bristol Entertainments Centre.

Tuesday 10 April

West Riding Section: 21st AGM, to be held at the Griffin Hotel, Leeds, at 7.30 p.m.

Thursday 12 April

Thames Valley Section: AGM, followed by a talk by a speaker from HM Customs and Excise, to be held at the Beech Tree Hotel, Maxwell Road, Beaconsfield, Bucks, at 7.00 p.m.

Newcastle Section: **Change of arrangements.** The AGM will now be held on Thursday 12 April at the Lambton Worm Hotel, Chester-le-Street, Co. Durham at 6.30 p.m.

Friday 13 April

Manchester Section:
Change of venue. The AGM will now be held at the University of Manchester Institute of Science and Technology, Renold Building, Room R/B 28, at 6.30 p.m.

Midlands Section: AGM, to be held at the Birmingham Chamber of Commerce and Industry, 75 Harborne Road, Birmingham, at 6.30 p.m.

Wednesday 18 April

Scottish Section—Eastern Branch: "Restoration and conservation" by Mr R. L. Snowdon of the Restoration Centre, Department of the Environment, Edinburgh. If possible this meeting will be held at a site where work is under way.

Friday 20 April

Irish Section: AGM, followed by an open forum discussion. To be held at the Clarence Hotel, Dublin, at 8.00 p.m.

Friday 27 April

Bristol Section: AGM, to be held at the Royal Hotel, Bristol, at 7.15 p.m.

West Riding Section: A dinner at the Bodington Hall to mark the 21st Anniversary of the Section.

May

Irish Section: Treasure hunt and golf outing. Details to be announced.

West Riding Section: Luncheon lecture. Details to be announced.

Thursday 3 May

Thames Valley Section—Student Group: "Corrosion inhibitive pigments." Speaker to be arranged. To be held at the Main Lecture Theatre, Slough College, at 4.00 p.m.

Monday-Thursday 21-24 May

OCCA-25. Twenty-fifth (Silver Jubilee) Technical Exhibition at Empire Hall, Olympia, London.

SILVER JUBILEE OCCA 25 OLYMPIA·LONDON·MAY·1973

Monday 21 May

Exhibition Dinner at the Savoy Hotel, London, WC2. Informal dress, 7.00 for 7.30 p.m.

June

Tuesday-Saturday 19-23 June

OCCA Conference: *Towards 2000* at the Grand Hotel, Eastbourne, Sussex, England.

Friday 22 June

AGM of the Association at the Grand Hotel, Eastbourne at 2.15 p.m.

Oil and Colour Chemists' Association

President: A. W. BLENKINSOP, F.T.S.C.

General

The Oil and Colour Chemists' Association was formed in 1918, to cover paint, printing inks, pigments, varnishes, drying and essential oils, resins, lacquers, soaps, linoleum and treated fabrics, and the plant, apparatus and raw materials useful in their manufacture. In 1924 it absorbed the Paint and Varnish Society. The stated purpose of the Association is to promote by discussion and scientific investigation the technology of the industries concerned with the above-mentioned products, and to afford Members opportunity for the interchange of ideas. This is achieved by the regular holding of ordinary meetings at which papers are presented, and the organisation of annual technical exhibitions, biennial conferences, educational activities and practical co-operative experimental work. Details of these activities are given in the *Journal of the Oil and Colour Chemists' Association*, which is published monthly, and whose pages are open to receive communications and other pronouncements on scientific and technical matters affecting the Members of the Association and the industries concerned. The Association's meetings also afford opportunities for Members to meet informally and socially.

Sections

There are Sections of OCCA in Auckland, Bristol, Hull, Ireland, London (with a Southern Branch), Manchester, the Midlands (with a Trent Valley Branch), Newcastle upon Tyne, Scotland (with an Eastern Branch), South Africa (with Branches in the Cape, Transvaal and Natal), Thames Valley, Wellington, and the West Riding, and these are responsible for the conduct of their own local affairs. There is also a General Overseas Section. There is also a close alliance between the Association, the Federation of Societies for Paint Technology in the United States, and the Fédération d'Associations des Techniciens de l'Industrie des Peintures, Vernis, Emaux et Encres d'Imprimerie de l'Europe Continentale (FATIPEC). The Association also maintains cordial relations with the Scandinavian Federation of Paint and Varnish Technicians (SLF).

The five Sections previously maintained by the Association in Australia formed (1.1.68) the Oil and Colour Chemists' Association Australia, having the same aims and activities as, and working in close liaison with, the parent body.

Membership

Ordinary Membership is granted to scientifically trained persons, and Associate Membership to others interested in the industries covered. An optional Professional Grade, conferring designatory letters, is open to Ordinary Members. Student membership is open without restriction to persons under the age of 21 and to those up to 25 who are following a course of technical study. The annual subscription in each case is £5.25, except for registered Students, whose subscription is £1.05. An entrance fee of 50p is payable by all members. Applications for membership are invited from suitably qualified persons who are engaged or otherwise interested in the industries noted above. Applications, which should be supported by two Members of the Association (one of whom must be an Ordinary Member), should be forwarded to the Director & Secretary at the address given below. Application forms and full details of membership may be obtained from the offices of the Association.

Professional Grade

The Association recently introduced (1971) an *optional* professional grade for its Ordinary Members, giving the designatory letters FTSC (Fellow in the Technology of Surface Coatings), ATSC (Associate in the Technology of Surface Coatings), and LTSC (Licentiate in the Technology of Surface Coatings). Full details are available upon request from the Association. Where Membership has lapsed, previous periods of Ordinary Membership count towards the total required under the regulations, as set out in the January 1973 issue of *JOCCA*.

Exhibitions

A technical exhibition is held annually at Olympia; Members are sent copies of the *Official Guide* several weeks in advance, in order to plan their itineraries. Non-members should apply, in writing, to the Director and Secretary for copies of the *Official Guide*.

Conferences and Symposia

The Association organises large, biennial technical conferences, the papers for which (together with discussions) are published in the Journal. Sections of the Association, in the UK and abroad hold symposia and these, too, are reported in *JOCCA*.

Publications

Journal of the Oil and Colour Chemists' Association (*JOCCA*) is published monthly and includes a yearly index in the December issue. The subscription rate to non-members is £10.00 p.a. in the United Kingdom and £12.00 p.a. ($31) abroad (post free; payable in advance). Single copies may be purchased for £1.00 (£1.25 abroad).

Introduction to Paint Technology (Second Edition with additional chapter). With illustrations. 187 pages and index £1.00 (including postage).

Paint Technology Manuals (Parts 1, 2, 4, 5 at present out of print).

Part 1 "Non-convertible Coatings"

Part 2 "Solvents, Oils, Resins and Driers"

Part 3 "Convertible Coatings," Second Edition, pp. 350, £2.80

Part 4 "The Application of Surface Coatings"

Part 5 "The Testing of Paints"

Part 6 "Pigments, Dyestuffs and Lakes, pp. 340, £2.00

Part 7 "Works Practice," pp. 218, £2.40

Director & Secretary: R. H. Hamblin, MA, FCIS,
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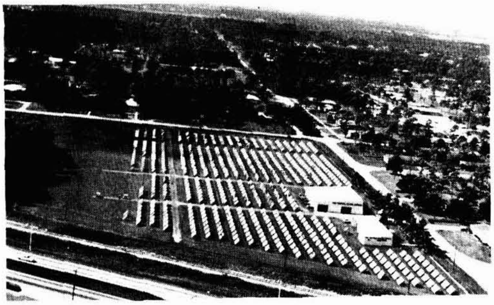

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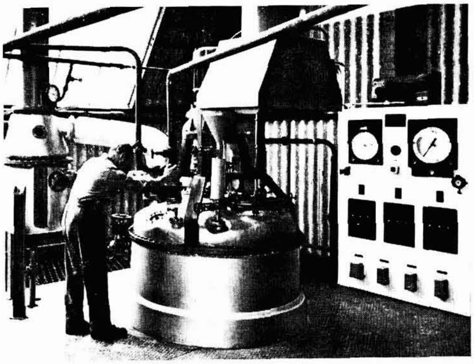

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Conference
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TECHNICAL EXHIBITION

Copies of the Official Guide are now available and are being sent to all Members of the Association and to those Non-Members who have already applied. Non-Members wishing to receive a free copy of the Guide should complete and send the form below immediately.

To: The Director and Secretary, Oil and Colour Chemists' Association, Priory House,
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