THE
PHYSICAL CHEMISTRY
OF PAINTS

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BY

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The Physical Chemistry of Paints

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PREFACE

As a result of experience in the teaching of Surface Coating Technology, I published in 1961 a small book called "Advanced Paint Chemistry".

This was an expansion of a series of articles written for students, in *Paint Manufacture*. It consisted entirely of organic chemistry. Even then, much that would be found in "traditional" text-books was excluded as it should have been studied previously.

Much to my surprise there was little criticism and indeed the first printing was sold out. Many friends made helpful suggestions which can be incorporated later.

This present book deals with the physical chemistry of paints. It has been, apart from any shortcomings of the author, a much more difficult book to write. The average paint student has little knowledge of physical chemistry (hence the absence of thermodynamics) and this has necessitated a more elementary approach.

At the opposite end, much of the work, for example on Corrosion and Rheology, is so highly controversial that the student would be confused were more than a resumé to be given.

It is hoped, however, that this book will not only give him a basic understanding of the general physical chemistry of surface coatings, but persuade him to make himself expert in one section.

If no more organic raw materials came on to the market, their loss would not be noticed. What is now required is a generation of physical chemists devoted to finding out why, for example, a powder covered with adsorbed water is wetted by an oil. The system then adheres, both in the wet film and in the dry polymerised film, equally well to hydrogen-bonded cellulose molecules or metals with distorted lattices, grain-boundary impurities and Heaven-knows-what adsorbed gases and liquids.

My good friend Dr. Ruzicka suggested that a section might be devoted to light. I hope I have complied sufficiently with his ideas.

As previously, I have given no references and indulgence is therefore asked for any details from publications, which have gone unacknowledged. I am sure that their authors would wish for their ideas to be widely known among students.

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My best thanks are due to my late colleagues, Mr. R. Mathews, who has made such a good job of the diagrams and Mr. V. Matthews, who read much of the physics, and I owe a debt to anonymous typists at Leonard Hill, who transcribed my scrawl.

In the previous book, I welcomed suggestions and criticisms. Now again, I repeat my request since, as in all teaching, "the student comes first".

INTRODUCTION

SUBSTANCES when pure exist in three primary states: solids, liquids or gases. Stable substances can generally be obtained in all three forms providing the appropriate conditions of temperature and pressure are provided. There are in addition to these states mixtures which may range from coarse dispersions, like the Chesil Beach, to smokes, foams and jellies.

Matter behaves in an orderly manner, to produce molecular and ionic structures of great regularity. Conversely, it behaves in a completely chaotic manner forming disordered masses bounded only by their containing vessels or the gravitational pull of the bodies in their neighbourhood. The first is exemplified by a crystal and the second by a gas in a cylinder, or the atmosphere of the sun.

Disorder allows atoms, molecules and ions complete freedom to move, vibrate and rotate; order places a constraint upon such movements and energy is, therefore, "locked up" in any regular system. If a spontaneous change takes place in such a system, the energy is released. This energy is known as entropy and it can be seen, firstly, that it will tend to increase, providing there are no ways in which it will be absorbed and, secondly, that if anything is known about the entropy of substances, it is possible to prophecy what a system is likely to do if changes occur. This will be considered at greater length when dealing with dispersions.

1

THE SOLID STATE

Solids built up in a regular way are called crystalline; those displaying no regularity, amorphous. Between these are the great mass of polymers, partially crystalline and partially irregular, referred to previously (Advanced Paint Chemistry, p. 77 *et seq.*).

Crystals can normally be so described by examination visually or under high magnification, but the ultimate criterion of crystallinity is their internal structure as shown by X-ray diffraction. If white light shines on a series of fine lines (a diffraction grating) arranged parallel to each other, a spectrum is produced. It has been found that X-rays can be diffracted by a crystal in a similar manner. As X-rays have frequencies approx. ten thousand times those of visible light, it is deduced that crystals consist of a similar arrangement of "parallel fine lines"—probably the atoms or ions themselves in the form of a three-dimensional lattice. Over the past half-century, evidence has grown supporting this idea, and the structure of crystals has been worked out.

Crystal types

Four main types of crystal have been recognised:
(*a*) Ionic.
(*b*) Co-valent.
(*c*) Metallic.
(*d*) Those involving intermolecular forces.

(*a*) *Ionic type.* Here ions are held together by the electrostatic charges resulting from the donation or acceptance of one or more electrons.

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The charge so transferred must be imagined as spread out over the whole ion and not existing as a point. The ions do not exist in pairs but pack together in a manner largely determined by their relative volumes.

Thus, referring to a cubic crystal there are three possible arrangements:

(i) Simple cubic structure (*Figure* 1).

(ii) Face-centred cubic structure (*Figure* 2). In this case each ion is surrounded by six ions of the opposite polarity; an example is sodium chloride.

(iii) Body-centred cubic structure (*Figure* 3). Here each ion is surrounded by eight of the opposite polarity; an example is calcium chloride.
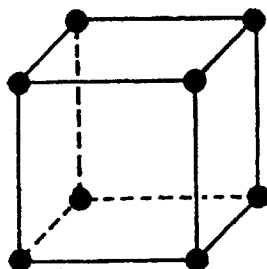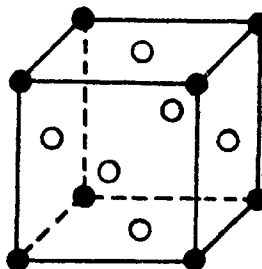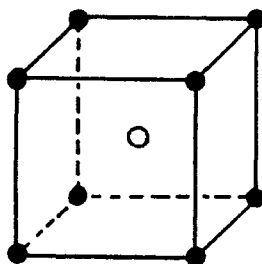

Fig. 1

Fig. 2

Fig. 3

(*b*) *Co-valent type*. In this class the atoms are held together by electrons shared between them. Hence crystals of this type are really giant molecules.

A typical example is the diamond crystal (*Figure* 4) where each carbon atom is bound to four others in a regular design, the distance between adjacent atoms being equal (1·54 Ångstrom units).
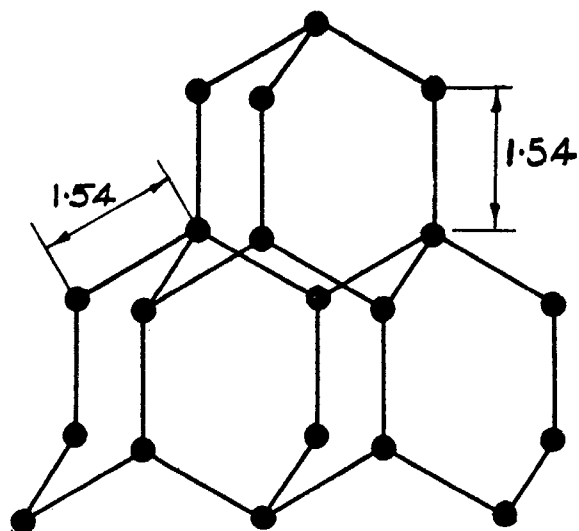

Fig. 4

Graphite on the other hand has a different structure (*Figure* 5). It consists of a planar network of hexagons, but the distance between the atoms in the hexagons (1·42Å) is less than that between atoms in adjacent layers (3·4Å).

(c) *Metallic type.* Metallic substances are believed to consist of ions, either of one or more metals, but the electrons, instead of being localised as in ionic crystals, exist as a cloud; hence the electrical conductivity associated with metals.

(d) *Crystals involving intermolecular forces.* As pointed out previously (A.P.C., p. 77) organic molecules often exist in a zig-zag style. If hydrogen bonding or van
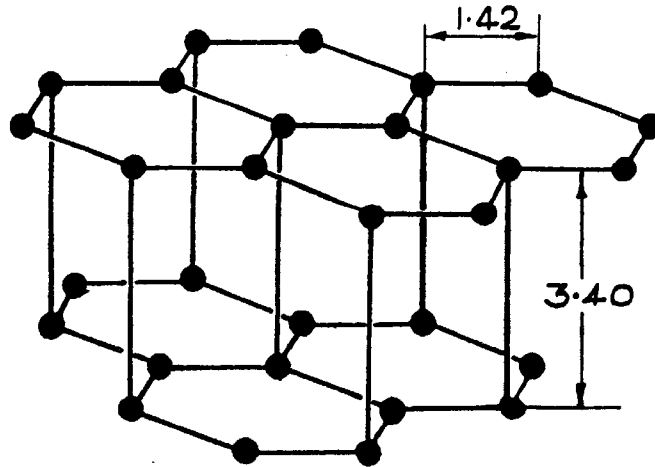
Fig. 5

der Waals forces exist between atoms in such a way as to cause a regular repeating arrangement to exist, then the substance is crystalline.

Crystallographic classification

Crystals have been classified by crystallography into groups depending on their symmetry rather than their internal atomic arrangements.
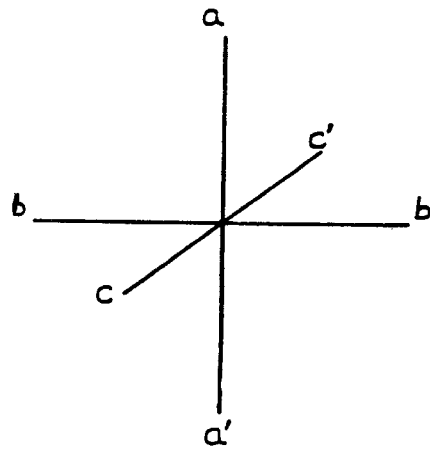

Fig. 6

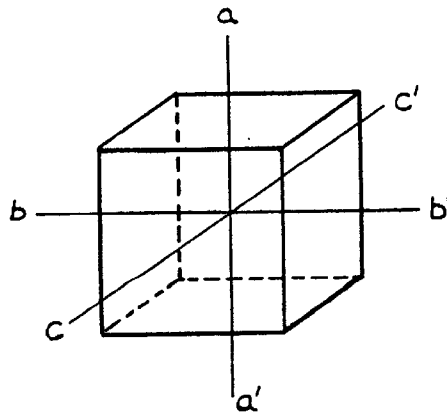If in space there are three axes aa', bb', and cc', they may be represented as shown in *Figure* 6.
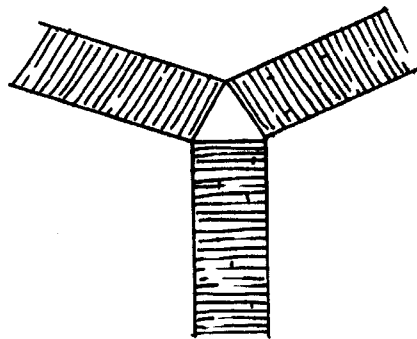

Fig. 7

Fig. 8

Crystals may, therefore, be classified as:

(a) *Cubic*. In this case the axes are at right angles and are all of the same length (*Figure* 7). Each face is at right angles to the axis and each cuts an axis at an equal distance from the centre. This is not to say that the edges may not be replaced by other faces, as shown in *Figure* 8. These faces do not affect the internal structure. Example: alum.

(b) *Tetragonal.* The axes are at right angles, but only two are equal (*Figure* 9). Example: tin.
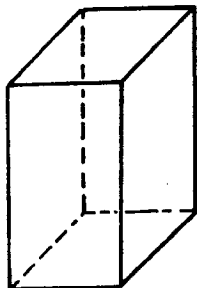
Fig. 9

(c) *Rhombic.* The axes are still at right angles, but are of unequal lengths (*Figure* 10). Example: sulphur.
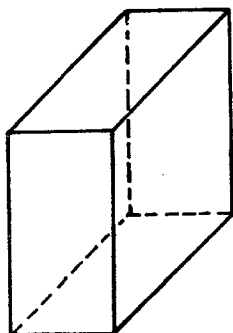
(d) *Monoclinic.* Two axes are at right angles with all three of unequal length (*Figure* 11). Example: sulphur.
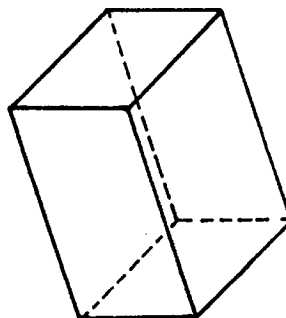
Fig. 10   **Fig. 11**

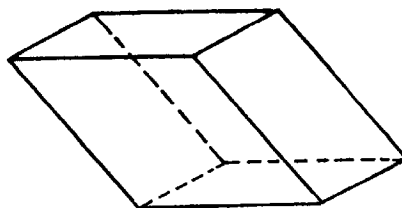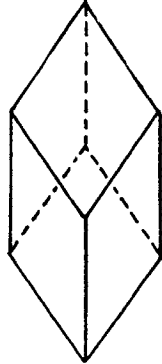(e) *Triclinic.* No axes at right angles and all of different lengths (*Figure* 12). Example: copper sulphate penta-hydrate.
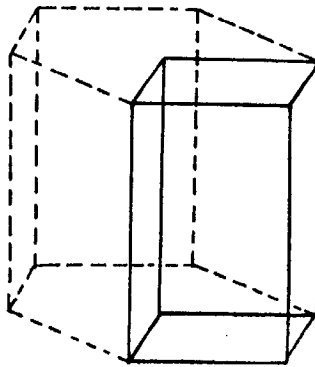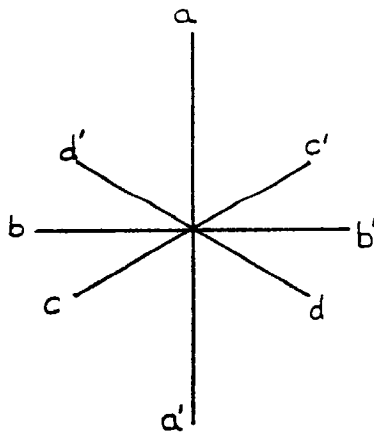
Fig. 12

Fig. 13

(*f*) *Rhombohedral.* Axes inclined obliquely at equal angles, with all axes equal (*Figure* 13). Example: sodium nitrate.

Fig. 14

(*g*) *Hexagonal.* In this system the vertical axis is at right angles to three axes intersecting at 60°, these latter being equal in length (*Figures* 14 and 15). Example: quartz.

Fig. 15

Supercooled liquids

Many substances classed as solids are in fact supercooled liquids. Others such as glass may resemble supercooled liquids in having no melting point but are prevented from crystallisation because the unit of structure does not repeat itself with sufficient regularity to allow crystallisation under normal cooling conditions.

A few crystalline substances can be obtained as supercooled liquids if prepared under dust-free conditions, but will crystallise if a crystal of the substance is added. This is a further example of the order—disorder relationship, order only being established by the addition of successive ions to an existing ordered structure.

Pigments

In the paint industry the chief value of crystalline substances is as pigments, and there are four important factors to be considered. The first is the refractive index relative to that of the medium in which the pigment is suspended. The second is the colour, the third the dimensions of the particles, and the fourth the chemical stability of the particles in the medium.

Opacity in dark-coloured pigments is a function of the ability of the particles to absorb light. White and light-coloured pigments have a relatively low absorption and depend for their opacity upon the ability of the particles to scatter light. This scattering power is dependent on the difference in refractive index of the solid pigment and the dried medium. There is also an optimum particle size for maximum scattering, and for substances with a high refractive index, such as titanium dioxide, this is approx. 0·3 microns.

The question of colour has already been dealt with for organic compounds (A.P.C., p. 149). Most inorganic substances are colourless, though due to differences in refractive index between solid and medium, many appear opaque and are used as white pigments. In general, the coloured pigments are compounds of the transition elements. In this class are salts such as chromates, and co-ordination compounds, *e.g.* Prussian blue.

In each case the element reacts by employing electrons in inner orbits. For example, iron has an electron configuration of 2·8·14·2. It therefore forms ferrous salts by loss of the two outer electrons. On the other hand, it can utilise the inner orbit to form the ferrocyanide ion, $Fe(CN)_6{}^{4-}$.

Particle size

There are two important criteria in particle size: the volume of the particle and its surface area. However, before attempting to show how these factors are determined, it is important to note their distribution among a population of particles.

Frequently, specifications may state that not more than say 1% of any bulk of powder passing a 300 mesh sieve shall be retained on 100 mesh. That is, particles approx. three times the diameter of the main bulk may not exceed 1% by weight, or a negligible proportion of the number of total particles. If the 1% refers to

number of particles, then 21·4% of the total weight is oversize.

Generally speaking, this type of size specification is satisfactory for ordinary powders, as it acts as a check on the behaviour of sieving systems operating on standard comminution machinery. However, even 1 % of oversize particles may ruin a polishing powder.
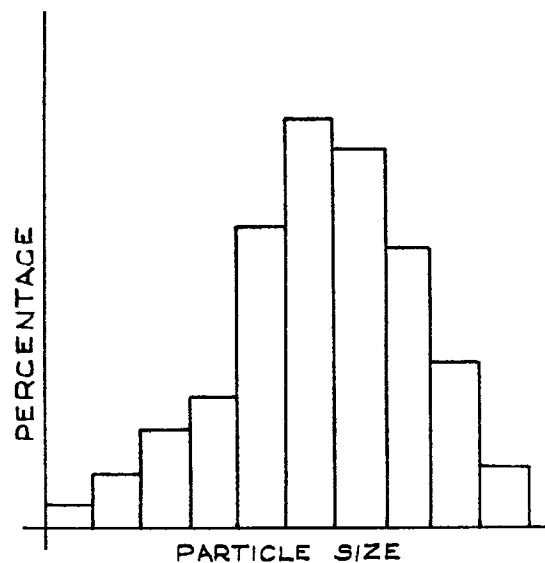

Fig. 16

At the other end of the scale, 1 % by weight of undersize particles of say 10% of the required diameter will mean that 91 % of the total number of particles will be undersize. This will mean a different rate of sedimentation, a different packing arrangement of the sediment (possibly leading to stirring troubles), and an increase of 110% in the surface area, which will affect the oil absorption of a pigment, the solution of a solute, or the reaction rate of a particle.

It is, therefore, not only important to know the dimensions of the particles but also the mathematical

distribution of various sizes in the bulk. This distribution may be shown graphically employing a histogram as in *Figure* 16.

Alternatively, a curve may be constructed (*Figure* 17). In each case the sieve size is represented on the abscissa and the weight or number of particles on the ordinate.

The shape of these curves gives an indication of the dimensional properties: a narrow curve shows consistency of size; a wide one, a divergence of size.
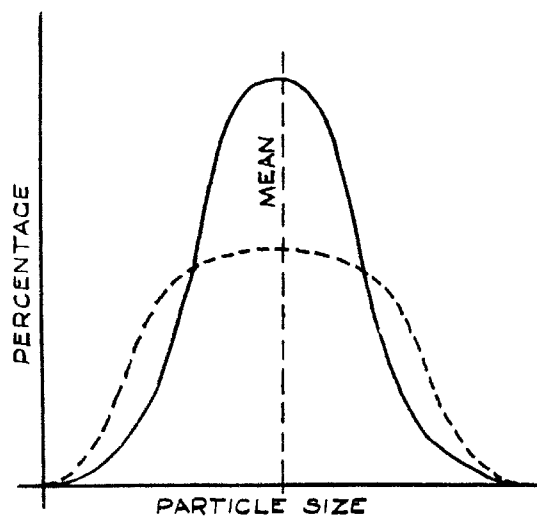
Fig. 17

Particle number and size determination

Methods of determination of particle number and size are described below.

1. *Sieving methods.* These generally involve determination of the weights of powder retained on sieves whose mesh sizes are specified by various national bodies. Sieving must be carried out under standard conditions of time and vibration to be satisfactory. While suitable for regularly shaped particles such as spheres and cubes, sieving is unsatisfactory for plates and particles of other shapes differing widely in planar dimensions, as large

particles may pass through diagonally. This can be seen from *Figures* 18 and 19. The results are usually given in weights of the various sizes separated.
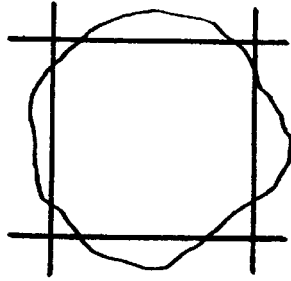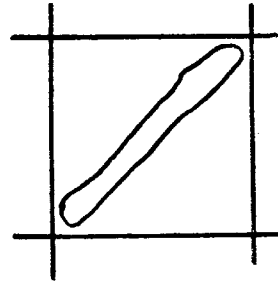
Fig. 18   Fig. 19

2. *Sedimentation.* If a small sphere of radius r is suspended in a liquid of viscosity η, it will sink at a rate depending, obviously, on the difference in density of the sphere and the liquid. It is also obvious that as between various liquids, it will fall at rates depending on their viscosities. Stoke's Law summarises these criteria into one equation, giving the rate of fall as $u = \dfrac{2gr^2(\rho-\rho')}{9\eta}$

where g is the acceleration due to gravity and ρ and ρ' are the respective densities of sphere and liquid. For any pair of liquids, therefore, $u \propto r^2$, but $u = \dfrac{\text{distance fallen}}{\text{time}}$

so that the distance fallen by any number of particles in the same time will be dependent on the radius of the particle.

If a long vertical cylinder is filled with a mixture of liquid and a small amount of powder (to minimise effects between particles), then at any level, analysis will enable a size range to be obtained.

3. *Elutriation.* If instead of allowing the particles to fall, a current of fluid is employed flowing at the same

rate as the particles would fall, then the particles would remain stationary. Particles of greater radius, however, would fall and smaller particles rise.

This is the principle of the elutriator, a number of types of which are on the market. They are particularly useful for the analysis of particles in the sub-sieve range.

The fluid used may be a liquid, generally water, or a gas, generally air. A typical elutriator consists of a number of cylindrical vessels of increasing diameter (*Figure* 20), so providing a lower rate of flow and hence a separation.
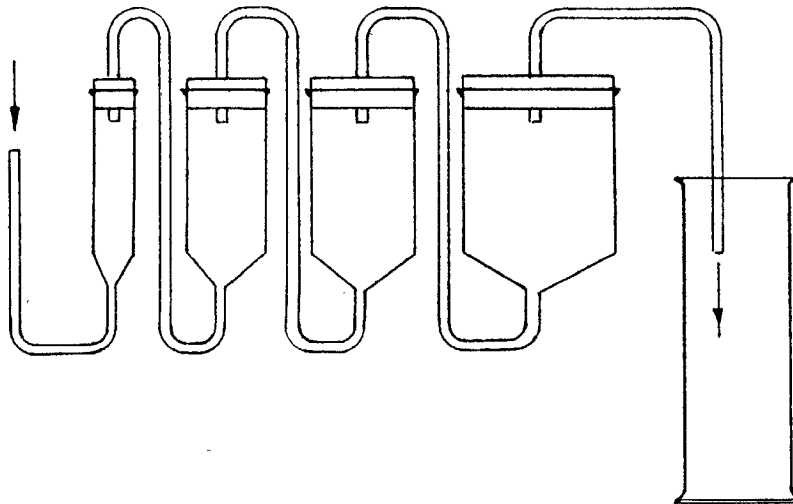
Fig. 20

In either of these methods it is necessary to carry out a count of the particles concerned and to measure their dimensions as few particles are spheroidal. This can be done by examining them with a microscope, or in extreme cases an electron microscope. Alternatively, the original powder may be examined.

4. *Light extinction methods.* In these procedures, a beam of light is projected through a suspension on to some form of photometer. A zero is obtained by using

the clear liquid, and a suspension is made by dispersing the powder uniformly in the fluid. Readings are then taken at intervals. The suspensions become progressively less opaque as the particles fall so that it is possible by mathematical analysis to obtain a size frequency curve.

Surface area

In the surface coating and related industries, particle size is of importance only in so far as it may influence gloss, or by breaking the surface lead to film failure. The more important property is surface area.

The specific surface is the area of surface per unit of weight. For instance, carbon black may have an area of up to 1,000 sq. m. per g. (or approximately 10 g. for the area of a football pitch). On the other hand, lithopone has a specific surface of 2·3 sq. m. per g.

Surface area has enormous effects. For example:

(i) High surface area would suggest high oil absorption.

(ii) High surface area with active pigments, such as white lead or zinc oxide, will mean rapid formation of large "soap particles".

(iii) Physical effects on the rheology of the system by attraction or repulsion forces at the solid-liquid interface.

However, the term "area" in any connotation is meaningless unless it is understood with reference to the method of measurement. The external area of a particle is easily measured by a number of methods. There is, however, an "internal" area, due to cracks, defects or pores.

It is obvious that if the size of such imperfections approaches the molecular dimensions of the fluid with which the particle is in contact, then the apparent area will differ from that measured by molecules of a different size.

This difference in external and internal surface for diatomaceous earth ranges from 4,790 sq. cm. per g. using a photoextinction method to 67,000 sq. cm. per g. using a nitrogen absorption method, *i.e.*, a ratio of 1:14. It has been stated, however, that ratios of 1:100 have been observed.

The three chief methods of measuring surface area are:

(i) Adsorption from a liquid phase;

(ii) Adsorption from a gaseous phase;

(iii) Permeability.

Adsorption methods

A particle is usually assumed to have a surface on which are adsorbed various gases and moisture. If a fluid is in contact with this surface, and the surface is wetted by the fluid, then the surface layer is either displaced by the fluid, or the latter attracted by the surface layer. In either case, if the size of the fluid molecule is known, then providing a monomolecular layer can be developed, the specific surface can be obtained.

The oil absorption technique practised in paint and ink laboratories is a rough and ready attempt to carry this method out, but expresses the answer in different terms. Any such method is doomed to failure as an exact procedure, due partly to the difficulties of wetting the surface and partly to the mechanics of dispersion.

A better method is to dissolve a solute, such as a dye, in the fluid and then to measure the diminution in colour of the solution resulting from adsorption by the solid particles under examination.

Another method employs a solution of a fatty acid in a solvent, the solution being analysed by titration before and after the adsorption. In this case, oleic acid of approximate molecular area 20·0 sq. Å. is used.

This non-mechanical method has the advantage that vacuum-dried powders, free from an adsorbed layer can

be employed. By choice of the correct adsorbed substance, an approximate area corresponding to the ordinary surface coating area can be obtained.

An accurate method is by adsorbing a non-reactive gas such as nitrogen at constant temperature, *i.e.*, the nitrogen isotherm. The temperature employed is usually in the neighbourhood of –190°C. The quantity adsorbed can be measured by weighing the adsorbent before and after adsorption, or by measuring the volume changes. While this method gives fairly reliable results, it must be emphasised that these bear little or no relation to the surface available for large oil or polymer molecules.

Permeability methods

If a powder is packed into a container and gas passed through, it is found that there is a difference in pressure between the inlet and outlet gases, and that this is related to the external surface, which can then be calculated.

2

THE LIQUID STATE

While the solids in surface coatings undergo on the whole practically no physical and very little chemical change, the liquid portion is constantly changing. Dispersions of solids, liquids, or gases in liquids (that is, the main bulk of finished products in the paint and ink industries) also have properties dependent on those of the liquid phase, and therefore simple liquids will be studied in this section, the rheology of dispersions being left until later.

A liquid is a substance whose molecules are in a state of disorder, similar to a gas, but owing to the cohesive forces between the molecules, it has under specific conditions of temperature and pressure a definite volume, even though it is not contained in a closed vessel. Pure liquids have the following properties:

    (i)   Vapour pressure.
   (ii)   Latent heat of vaporisation and solidification.
  (iii)   Viscosity.
  (iv)   Surface tension.
   (v)   Optical properties.
  (vi)   Dielectric constant.

Vapour pressure

Assuming that a quantity of liquid is in a container with an evacuated space above it, then the following phenomena can be visualised. The temperature will be, say, 25°C. Molecules of liquid will be in motion, at different velocities. Most of them will be held by the

cohesive forces between the molecules, but some with higher velocities will escape into the free space above the liquid. There will be a continuous movement out of the liquid, but as time goes on, some of the molecules moving about will strike the liquid surface and return to the main bulk. Providing there is always some liquid present, there must come a point at which there is an equilibrium between the number of molecules entering and leaving the surface.

The molecules in the free space bombard the sides of the vessel, that is they exert a pressure. As equilibrium has been attained, this pressure must be characteristic of the liquid at that temperature and is known as the saturated vapour pressure. Molecules that have left the liquid have a greater kinetic energy than those left behind, and as this energy finds its origin in the heat content of the liquid, the temperature of the latter falls. If external heat is now applied, this will be absorbed in bringing the system back to 25°C., and is known as latent heat.

These relationships are extremely important in spraying paints. Let us assume that a film is being sprayed. The solvent molecules, having a free space containing few or no molecules of their species,will move continuously from the liquid, and the temperature of the latter will fall rapidly. Water vapour at the surface of the deposited film will be cooled, and if its vapour pressure is higher than the saturated vapour pressure of water at this temperature, then liquid water will be condensed on the film. The water gives up its latent heat to the film and in consequence more solvent is evaporated. The viscosity now increases and the water is locked in mechanically: "blushing" is said to have occurred and the finish is ruined.

Latent heat

Molecules of vapour have a greater degree of disorder than those of the liquid; consequently, there is an increase

in the entropy of the system when evaporation takes place.

This increase ΔS is equal to L/T, where L is the latent heat of evaporation and T the temperature in °K. When the vapour pressure of a liquid reaches atmospheric pressure, the substance boils. The increase of entropy on boiling is given by

$$\Delta S = L/T_b$$

where T_b is the boiling point.

The vapour pressure of a liquid is lowered, *i.e.*, the boiling point is raised, when a substance is dissolved in it. The rise in boiling point is characteristic of the solvent and the molecular weight of the solute:

$$\Delta = \frac{Kw}{MW}$$

where Δ is the rise in boiling point, w is the weight of solute, K is a constant characteristic of the solvent, W is the weight of solvent, M is the molecular weight of the solute.

In the surface coating industries, M is usually very high and therefore changes in vapour pressure are small.

The vapour pressures of solvents are not usually measured in these industries directly, use being normally made of their comparative rates of evaporation against a standard solvent, such as diethyl ether or butyl acetate.

If two liquids are mixed and distilled, the boiling point of the mixture will normally rise from that of the first liquid to that of the other, and by the use of efficient fractionating coluums pure samples of each may be obtained. If, however, the boiling point curve passes through a maximum (*e.g.*, acetone and chloroform) or a minimum (*e.g.*, propanol and water), then under the same pressure, mixtures having the composition at these points cannot be separated by distillation.

Such mixtures are called azeotropes. Mixed solvents, such as are generally employed for non-convertible coatings, may have higher or lower rates of evaporation than their individual constituents.

Related to the vapour pressure, but also to composition and thermal stability, is the flash point of a liquid. No satisfactory theory has been worked out that will enable this to be calculated, but within limits, the flash point of a mixture is that of the component with the lowest flash point.

Viscosity

The cohesive forces between molecules not only prevent them leaving the liquid but also impose restrictions to movement within the liquid. Let us assume that a liquid is flowing along a rectangular trough so wide that
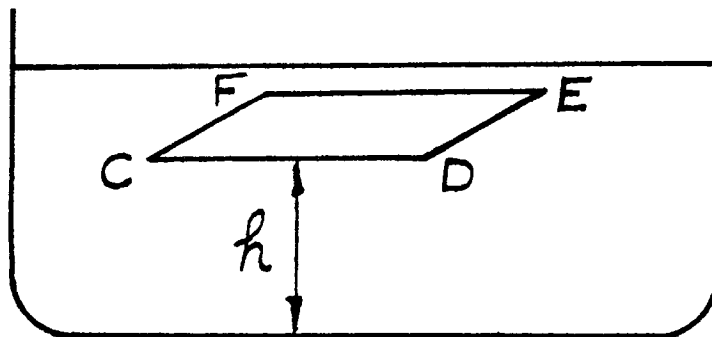
Fig. 21

"drag" from the sides is negligible, and the liquid at the bottom is at rest, then there is a velocity gradient from the surface to the base depending on the distance, h, from the base.

If a plane CDEF parallel to the base is now considered (*Figure* 21), molecules above this will accelerate the molecules in it and those below will retard them. Assuming that CDEF is a square of side 1 cm. and the

thickness x is negligible, then the tangential force acting on either side of the plane will be given by the expression

$$F = \frac{\eta v}{x}$$

where v is the difference in velocity on the upper and lower faces of CDEF. If x is large, edge effects will arise.

The term η is known as the coefficient of viscosity. It is measured in dynes per sq. cm. per unit velocity gradient. This unit is termed the "poise" in honour of Poiseuille.

Measurement with such a system is extremely difficult and the viscosity is normally obtained by measuring the flow of a liquid through a capillary tube. Poiseuille's formula forms the basis for such measurements:

$$\eta = \frac{\pi r^4 p t}{8vl}$$

where r is the radius of the tube, p is the driving pressure, t is the time of flow, v is the volume of liquid, l is the length of the tube.

The driving pressure p is obtained from the difference in hydrostatic head, h x d x g, where d is the density and g the acceleration due to gravity.

Modifications of the capillary tube method are commonly used. In modifying this equation to include the viscosity of a real fluid, it is convenient to consider the ratio

$$\frac{\text{coefficient of viscosity}}{\text{fluid density}}$$

This quotient is the coefficient of kinematic viscosity and is measured in stokes. For very viscous liquids use may be made of Stoke's law:

$$v = \frac{2}{9} gr^2 \cdot \frac{(d-d_1)}{\eta}$$

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