Dispersion techniques in the Paint and Allied Industries

By I. Berg, sometime process development manager, Berger Paints

A joint symposium under the auspices of The Institution of Chemical Engineers (North Western Branch) and the Society of Chemical Industry (Manchester Section) was held on September 24, 1975, the subject being "Manufacture of Industrial Solid-Liquid Dispersions, Art or Science?" Although other learned societies were associated with the venture, only two papers dealing with dispersion techniques in industry were presented. Mr G. Hayes (Salford College of Technology) gave a paper on "Dispersion techniques in the food industry", while the writer dealt with the paint industry. The other papers were concerned with the physical chemistry of solid-liquid dispersions and the choice of equipment.

Such symposia highlight a cavalier attitude to dispersion techniques and emphasise a general reluctance to appreciate the principles involved. In part, blame may be apportioned to classical colloid chemistry concepts based on "infinitely dilute" suspensions, although in the last few years some effort has been made to understand concentrated products. Methods of preparation, however, still appear to be neglected. It is intended to show, therefore, that strict attention to detail is necessary when making these concentrated suspensions if repeatable results are to be obtained, and unless this is realised no amount of theory can be valid. The simple principles of obtaining satisfactory and repeatable dispersions will be established so that only minor modifications are required for application to the many different types of equipment available.

The basic problem

It is advisable to consider the basic problem as the complete dispersion of a particulate solid in a given liquid, such that the solid will be broken down into the single particles which will be fully wetted by the liquid. It will be shown that even if a complete dispersion is not required and only a partial dispersion will suffice, it is still advisable to start as for a complete dispersion and stop at an early stage rather than modify the conditions at the beginning of the process.

The solids in question are actually aggregations of clusters of particles, many of which are so small that the whole would behave as smoke were it not for the fact that a degree of cohesion is exhibited. The latter is in part a result of the manufacturing process and partly due to the "impurities" such as moisture, gases and grease adsorbed on the surface of the particles. The dispersion process is therefore not a comminution process but resolves itself into a separation procedure, immediately followed by a wetting action which effectively replaces the impurities on the surfaces by the liquid.

In the manufacture of some of the particulate solids, however, heat may have to be applied such as in a drying process. If sufficient care is not exercised, or if the economics of the process does not permit the amount of care necessary, some sintering can occur between two (or even more) adjacent particles. If the sintering area is very small, e.g. pinpoint, then the ease of dispersion may not be affected. If, however, the areas are larger, difficulty will increase until, with whole surfaces sintered, two particles may effectively be fused to behave as one larger particle. In a poorly prepared particulate solid raw material, it is therefore possible to have the full spectrum —from the aggregates of easily dispersed particle clusters to agglomerates—which may be impossible to disperse in some machines and may require comminution.

Illustrative examples

The major principles of dispersion techniques may be readily demonstrated by considering three different dispersion procedures:

(a) The preparation of a very fluid mustard mix;
(b) The colouring of plastic materials;
(c) The pigmentation of powder coatings.

(a) When preparing a very fluid mustard mix it is necessary to start by adding to the whole of the powder only a small quantity of the liquid, certainly not enough to wet the powder noticeably. The whole is then mixed thoroughly to allow the particles to compete for the liquid and become equally wetted. When this is judged to be so—a matter of experience initially but eventually could be controlled by timing, dependent upon size of sample, size of vessel and rate of mixing—another small quantity of liquid is added to be followed by further efficient mixing so that the partially wetted particles can compete for the extra liquid. This is repeated until the whole mass has become thoroughly wetted by the continued small additions of liquid followed by intimate mixing. At this stage, which is usually fairly obviously well-defined, larger quantities of liquid may be added, with continuous mixing, at a rate to prevent free liquid floating on the surface until the required consistency is obtained.

If the whole of the above procedure is repeated with other batches of the materials, then, provided the properties of the latter are within agreed acceptable limits compared with the original materials, the results will be sufficiently comparable to the original trial to warrant approval as a satisfactory repeat.

At this stage it should be emphasised that repeat trial results can never be absolutely identical as the original, even if they appear to be so after various general tests. The latter are really a coarse evaluation compared with the sizes of particles.

Thus samples prepared from raw materials, taken from the same batches, prepared in the prescribed manner will generally have slight but obviously acceptable differences. This is because the general properties of the materials are statistical averages of the properties of the constituents, and where these are particles a "packing" effect may be expected.

Returning to the preparation of the mustard mix: if an attempt at a short cut is made by adding the powder to the whole of the liquid in one fell swoop, the result would be a mass of globules or clusters of powder floating in excess liquid. No amount of stirring at this stage is likely to yield an acceptably smooth mix. Moreover, if this latter procedure of plunging the solid into all the liquid were repeated, another mass of globules will be formed. This time, however, the clusters or globules will not correspond either in number or composition to those in the immediately previous mix. No matter how many times this latter method is repeated, the number and composition of the particle clusters and globules will be different.

The consequences of the above may now be briefly considered:

(i) The properties of the various products made by using all the liquid at once will not only differ from one another, because they are virtually different materials, but will also differ from the original "standard" controlled liquid addition product, prepared as described at the start of (a).

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(ii) It is obvious that the same materials processed in a similar manner may produce quite dissimilar products.
(iii) In order to obtain a reasonably repeatable result a specific procedure, in which random conditions are reduced to a minimum, must be followed.
(iv) Generalising (i) it can be deduced that any process deviating from the standard controlled non-random procedure will yield products differing from the standard and from one another.
(b) The colouring of a plastic material may be undertaken in one of a number of heavy-duty machines. The plastic and pigment may be subjected to very high shear stress in, for example, a twin-roll mill. The plastic is forced to flow by the pressure and therefore behaves like a very high viscosity fluid which shears the pigment clusters into smaller clusters and finally into primary particles. All heavy-duty machines can be provided with facilities for heating (or cooling), but heat to render the plastics less viscous must be used cautiously otherwise the final viscosity may be too low for adequate dispersion.
(c) The pigmentation of powder coatings is a process similar to (b) above. The heavy-duty machine in this case is an extruder/kneader combination. The resin, pigment and requisite additives are thoroughly premixed and passed into the machine via a hopper. The action forces the mixture through a heating area, partially to melt the resin to a very high viscosity fluid, then to the kneading section which again subjects the mass to a very high shearing stress which reduces the clusters to smaller clusters, and so on. The machine concludes its function by extruding the processed material. Here again a major problem is to avoid overheating if excellent dispersion is required, because reduction in viscosity would reduce shearing efficiency. This problem will be accentuated with the requirements of very fine powder coatings.

Conditions for dispersion

It is possible, from a study of the three dispersion trials described above, to develop a unified principle, on which can be based a generalised technique for dispersion, suitable for a wide variety of industries. Two common factors in the processes discussed can be abstracted:

1. High viscosity at least at the outset of the process.
2. Flow—either as a result of the physical properties of the material (i.e. molten or sheared resin or plastic) or as a result of an impeller (stirring the mustard: *N.B.* sheared resin or plastic can be regarded as under the action of an impeller).

It is the second factor—flow—that warrants extended study in the investigation, for without flow there is obviously no action.

In the study of mixing two major types of flow are postulated, viz. turbulent and laminar.

Turbulent flow enables massive interchange of material on the macro scale between various locations. Laminar flow, which is flow as nearly as possible in layers, involves interchange of material between adjacent layers at the micro (mainly molecular) level. The transition between laminar flow and turbulence is not well defined and often the practical conditions occurring in processes can be neither fully defined as turbulent nor properly defined as laminar. Indeed, this can be readily demonstrated in the action of the high-speed mixer (disperser) which, with given conditions, can indicate high turbulence at the impeller periphery and absolute laminar flow at the side of the tank. Thus both laminar and turbulent flow can exist in the same system, and obviously the regions between these two extreme conditions cannot readily be defined whatever theory is invoked!

Returning to the question of dispersion, it is seen that the flow in question with respect to the examples discussed could only have been laminar with little or no turbulence, i.e. firstly in the correct (and standard) method for the mustard preparation there could be no turbulence without excess liquid (there was excess liquid in the incorrect method and therefore turbulence which did not result in efficient dispersion); secondly, the flow of barely molten resin or plastic cannot be described as anything but laminar.

It is reasonable therefore to conclude that an important common factor for efficient dispersion is laminar flow. This is not to suggest that there is no dispersion at all in turbulent conditions. In the mustard experiment, when the solid is thrown into all the liquid, some dispersion had obviously taken place. It is possible that some regions, very localised, had exhibited laminar flow and therefore small pockets of efficient dispersion had occurred. The main effect, however, of the turbulent flow is an inefficient process for dispersion with results that are not really possible to repeat. (Note: Turbulent flow is ideal in conditions that require mixing processes as distinct from dispersion processes because massive interchange of material from one region to another is the requirement of good mixing.)

The major single condition for laminar flow is high viscosity. The latter was the other common factor in the experiments and therefore it appears that both factors are probably two different facets of the same principle. To bridge the gap between industries with high viscosity media (plastics) and the lower viscosity media (paint, printing ink, etc.) it is only necessary to stress that the obvious major condition for efficient dispersion is laminar flow induced either by the high viscosity of the continuous phase or by a high concentration of the particulate solid which will contribute more to the viscosity than the liquid. This theme will be subsequently developed in the consideration of dispersion techniques mainly in the paint/printing ink industries because the guide-lines thus established will be applicable to many other industries.

The paint and printing ink industries

The requirements in the paint and printing ink industries, with respect to the dispersion of particulate solids, are so all-embracing, that when met, constitute excellent guidelines for universal application with only minor modifications. It is therefore intended to discuss these industries in great detail with references to other industries as appropriate.

It has been stressed that the resins and other media used as the continuous phase in the paint industry are low in viscosity, compared with the barely molten materials in the plastics industry, and are often in solution. Therefore, in order to produce laminar flow for the most efficient dispersion, the high viscosity necessary has to be obtained by using as high a centration of the particulate solid (in this case the pigment) as possible. However, a limitation on the concentration may be imposed by the choice of the plant used. If the equipment is not of sufficiently sturdy construction very high viscosities may not be possible. Equally some machines have an action which may not be effective for high viscosities. These will be elaborated on when the specific machines are considered.

The insistence on a high pigment content in the preliminary dispersion formulation, to the extent that the pigment contributes far more to the viscosity than does the liquid, brings an added bonus. The induced laminar flow is actuated by an impeller and the velocity is probably logarithmically inversely proportional to the distance from the impeller. Thus adjacent layers have different velocities, i.e. not only is the flow laminar but differential which accounts for the shearing action. Added to the shearing action of the flow, however, the high pigmentation ensures that clusters of pigment in adjacent layers collide and result in a mutual shearing action, augmenting the dispersion to the greatest efficiency.

The particulate solids

The pigments used in the paint and printing ink industries are legion. Apart from the obvious general mass properties such as relative density, colour, reactivity and resistance, the specific properties of the primary particles are significant. These include size, shape, cohesiveness and general surface properties which

can be markedly affected by adsorbed impurities.

The shapes of the particles can often affect properties of prepared products, of which they form a part, and therefore their study can be crucial. However, when comparing particle sizes it is much simpler to consider the particles as spheres—of equal volume to the particles. Thus only one figure (the diameter of the spheres) need be used to compare the relative sizes of the particles of the different pigments.

Figure 1 illustrates the wide variety of particle sizes of some of the pigments used. It is obvious that some pigments have particle sizes 100-200 times (or more) the diameter than that of the particle sizes of other pigments. It will not be surprising if problems arose as a result of attempting to disperse mixtures of particles with such large variations in size. Considering the basic dimensions we have:

Ratio of particle diameters 1 : 10^2
Ratio of particle surface areas 1 : 10^4
Ratio of particle volumes 1 : 10^6
Ratio of numbers of particles to make up same total volume of material 10^6 : 1
Ratio of total surface area of the particles making up the same total volume of material 10^2 : 1.

It follows therefore that:

(a) When small quantities of the pigment with small particles are milled with large quantities of the pigment with large particles, precautions must be taken to avoid the situation when the small particles are shielded within the larger particle interstices and are not subjected to efficient dispersion;

(b) When equal volumes of two pigments of such dissimilar particle sizes are milled together, the requirement of the smaller particle size pigment for adequate wetting (i.e. replacing the impurities adsorbed on the particles' surfaces by the continuous phase) will be so great compared with that of the other pigment that the latter can be swamped if care is not taken.

Both the above problems will be examined in greater detail at a later stage, together with other relevant details such as the difference in the time of dispersing large and small particles.

The continuous phase and wetting

There are numerous types of materials used as the continuous phase (i.e. film former) comprising every type of resin, plasticiser and natural polymers including oils. The continuous phase—termed the medium or vehicle—often has the most profound effect on the properties of the completed dispersed material both in the container and after application.

The influence of the pigment or other particulate solid may vary from quite a comparatively minor role such as that for colouring only to fairly important parts such as:

(a) Protection from deterioration as a result of exposure, e.g. to U.V., I.R. and visible radiation;

(b) Protection from corrosion;

(c) Modification of rheology for specific application properties.

Whatever role the particulate solid is designed to play, however, the degree or efficiency of dispersion (and as a corollary, the degree or efficiency of wetting) will determine in no small way the success of the exercise. Although the simple definition of wetting previously given is probably the best for general purposes, some further thought could be helpful; for example, assume that in a suspension the particulate solid has been fully dispersed, i.e. every primary particle is completely separated from every other one and the space between is filled with the continuous phase, i.e. the vehicle. For stability it must be assumed that the particles are adequately wetted by the vehicle, i.e. that all the relevant impurities (vapour, dust, etc.) on the surface of the particles have been replaced by the vehicle. Such being the case only natural intermolecular motion, e.g. Brownian, will govern the degree of stability. If, however, the particles are not well wetted one can assume an additional imbalance of forces, accelerating settlement either on the bottom or sides of vessels, causing cohesion between particles with subsequent flocculation or even causing floatation.

Problems arising from inadequate wetting

It is not intended to discuss the scientific study of wetting here but to indicate some of the problems resulting from inadequate or partial wetting, i.e. as described in the paragraph above. On the other hand it is as well to mention some points that could indicate why the ideal results do not necessarily occur even with optimum conditions. For example it would be of interest to consider the physical picture presented by the action of wetting. If the molecule of the vehicle is larger than the pigment particle one can wonder whether the molecule will wrap round the particle or have just one end "touching" the particle. It is believed that several different possibilities of molecular arrangement are valid. A point of particular importance is whether the space around the particle permits enough access for the vehicle molecules to wet the surface adequately. Various configurations of the "wetting" molecules may aggravate the space problem.

One must also consider the stage of a pigment when not fully dispersed and the smallest "particle" is in reality a cluster of primary particles. These have behaved as one coherent particle congolomerate, the external surface(s) of which can be wetted in the usual way although the intersticial surfaces may not be affected. If the conglomerate remains entire during application, problems may be few although loss of gloss is conceivable due to repeated reflection and refraction on wetted and unwetted surfaces. If, however, high shear application breaks down the agglomerates, the unwetted surfaces could give rise to all manner of problems.

It is stressed that all the effects attributable to adequate or inadequate wetting or dispersion are so ascribed mainly by experience but also by inference. Thus although there is no doubt at all that the degree of dispersion permits no other interpretation than the extent to which the particulate solid has been dispersed, the writer has some reservations with respect to the strict

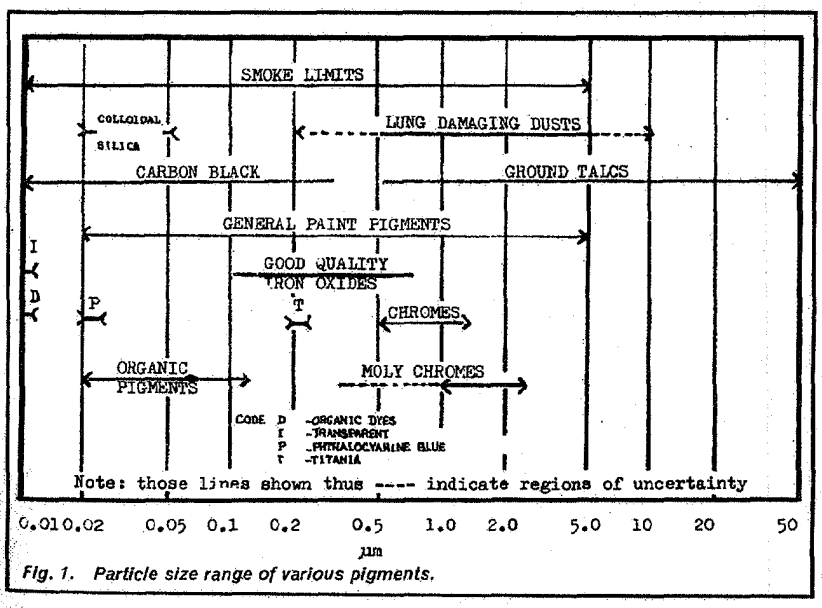


Fig. 1. Particle size range of various pigments.

definition of wetting. Indeed there is the possibility that all the adsorbed impurities need not be replaced (nor even should be replaced in entirety) to give the effect of adequate wetting. Although some (no doubt most) of the adsorbed impurities must be replaced by the wetting vehicle, the residue can act as a surfactant actually helping the dispersion process and becoming part of the particle/vehicle complex. Two examples are known widely:

(a) Absolutely dry titanium dioxide will not disperse as readily as that with the recognised amount of moisture present;

(b) Carbon blacks which have been stored a long time (and therefore had longer time to adsorb impurities) tend to disperse more readily than reasonably newer batches. Presumably the storage facilities determine the usefulness (or otherwise) of the adsorbate.

It is felt that other examples abound but investigation facilities are lacking!

Stabilisation

The object of a dispersion process is to obtain a stable base of the particulate solid in the vehicle. Unfortunately nothing is really stable and as soon as the mechanical forces in a dispersion process are stopped there is a tendency for the dispersed particles to meet, coalesce into larger masses, finally to settle or flocculate, nullifying all the original, costly procedures of separation. Therefore the words "stable" and "stability" can only be used in a relative sense denoting the useful life of a dispersion, or the period of time between the actual dispersion process completion and that when the dispersion prepared has deteriorated to the extent that it can no longer be used for the originally intended purpose.

Stabilisation is often incorrectly and inadequately carried out, sometimes neglected entirely and often used as an excuse for poor milling formulations. Its importance is such that it is being considered here before the actual milling formulations, as well as subsequently, at the relevant stages. It is assumed that the formulation being processed is satisfactory inasmuch as the basic components are not incompatible—otherwise gross instability will probably result unless mutually compatible additives are used.

As a general rule, however, four major factors determine the stability of a dispersion, viz.:

1. Pigment concentration. The higher the pigment concentration the more likely are the particles to meet (because of internal motion) and coalesce.

2. Degree of dispersion. The better the dispersion, i.e. the nearer the particulate solids are milled to their primary particles, the longer will be the time taken for their coalescence to sizes that would be detrimental to the final product.

3. Non-volatiles of the vehicle. For stability the particles must be adequately wetted by the polymer vehicle non-volatiles which also form a barrier between the particles.

4. Viscosity. The higher the viscosity or structure of the material the greater the resistance to internal motion and therefore the stability is improved because the particles are not allowed to meet easily.

Stable base formulation

If the above factors are combined with the requirements of production departments, it is possible with the aid of experience to formulate a reasonably stable base. The stability of the base must be such that if any emergency arose, the stabilised base, which normally would be processed to form a number of products just by the addition of resins and modifying additives, could be allowed to stand for about two months before deterioration reduces the usefulness. Furthermore compromises may be necessary because:

1. Pigment concentration. It is more economical for production to have bases with high pigment concentration although this is inimical to stability.

2. Degree of dispersion. More time spent on dispersion is uneconomical if a less well-dispersed material will satisfy the customer!

3. Non-volatiles and 4. Viscosity. Production favours both low non-volatiles and low viscosity for ease of handling.

It is therefore obvious that production requirements and stability factors are almost entirely mutually opposed. The necessity to balance the opposing factors can be very taxing.

As the pigments and vehicles have so many diverse properties it could appear that the ideal would be to have a different formulation for each pigment/resin combination. This is obviously impracticable. A generalised formula therefore has been devised to indicate the requirements for a stable base (Table 1).

The following points relating to Table 1 are relevant:

(a) The quantities given are based on the "oil absorption" of the pigment or other particulate solid (Note: oil absorption refers to the number of grams of a given vehicle used *just* to bind together 100 g of the solid);

(b) There is no theoretical foundation for the figures in Table 1 which are based on experience but which serve as an excellent guide;

(c) It is conceivable that some formulations will not fit in perfectly with the given figures, in which case the "best possible fit" should be used;

(d) Table 1, it is emphasised, refers to the type of formulations with which dispersions should be completed. The type of formulation with which the dispersion process should be started is discussed and indicated in the next section.

Initial dispersion (milling) formulation

The formulation with which the dispersion process is started must be such that laminar flow—for the most efficient results—must be ensured by high viscosity induced preferably by high pigmentation or other particulate solids. It is emphasised, however, that it would be futile to indicate the viscosity required for a variety of reasons:

(a) The viscosity is most unlikely ever to be Newtonian and therefore cannot under any circumstances be represented by a single point or figure.

(b) The relevant viscosity is that which appertains to the mill base during the process, i.e. while the mill is operating.

(c) The viscosity prior to milling invariably has a yield point.

(d) During the dispersion process the viscosity will change, indeed some authorities have considered the possibility of controlling the dispersion process by means of viscosity parameters. This is, however, quite unrealistic, although the viscosity of an organic pigment base will undoubtedly increase during the process, inorganic pigment bases are likely to indicate a decrease. Moreover temperature plays a profound part in the value of viscosity, while different batches of raw materials will indicate different viscosity interpretations if very critical assessments are required.

All in all, although the importance of viscosity is not to be decried in general,

TABLE 1. STABLE BASE FORMULATION

Particulate solids			
Oil absorption	Examples of types	Maximum concentration %	Minimum non-volatiles of liquids %
Low	Titanium dioxide: whiting: chromes: natural oxides	60-70	30-35
Medium	Synthetic oxides China clay	30-50	35-40
High	Organic pigments	15-30	40-45
Very high	High surface area pigments and extenders	10	45+

the major requirements for the initial dispersion formulation as denoted in Table 2 will compensate for the consistency of the material being processed.

Once again some qualifications must be noted with respect to Table 2:

(i) There is no theoretical basis for the table which is based on practical experience.

(ii) The pigment content has been deduced as a function of oil absorption.

(iii) Ranges of figures are given here as were given for Table 1.

(iv) As distinct from Table 1, it will be noted that two ranges are given for the liquid non-volatiles. This is because the vehicle required depends not only on the oil absorption of the pigment used but also on the method of dispersion. In order to avoid too complicated a table the processes are considered to vary from high shear rates to low shear rates and the figures for these are given. When shear rates between these extremes are used relevant intermediate figures would appertain.

(v) The pigment types representing the various oil absorption ranges will of course be the same as in Table 1.

It should be explained that the zero in the table shows that in particular circumstances, indicated at a later stage, the resin content can be nil, provided sufficient surfactants are present.

It must be emphasised that both tables are indications and must be regarded as preliminary guides. Variations in raw materials are such that a guide more definitive than these tables may tempt many to use it without due consideration to the basic underlying factors. This is to be deprecated simply because it would leave the dispersion practitioner in difficulties should some unexpected situation arise. Provided this intimation is accepted then the graph (Fig. 2) sums up the major requirements denoted in both tables which are considered advisable to retain in order to emphasise that the figures should not be accepted as absolute but as indications which may require modifications in certain cases.

Some notes specific to the graph in Fig. 2 are relevant:

TABLE 2. INITIAL DISPERSION (MILLING) FORMULATION

Pigment oil absorption	Pigment concentration %	Minimum non-volatile in liquids	
		%	%
Low	75–85	0–10	25–30
Medium	50–75	10–20	30–35
High	25–50	20–30	35–40
Very high	— 25	30 +	40 +

(1) The accuracy of the figures given towards the end of the oil absorption axis, i.e. beyond the figure of 200 is considerably reduced. It is doubtful whether oil absorption figures in that range can be reasonably accurately determined and whether there is any meaning in differentiation in that area. Certainly the curves denoting pigment concentration beyond an oil absorption figure of 500 should be continued parallel to that axis beyond the graph if necessary.

(2) The ranges of pigment concentration given in the two Tables (1 and 2) have been split up into four different curves:

(a) Premixing—high/low shear rates;
(b) Attritors—batch bead mills;
(c) Ball mills;
(d) Stable base—continuous mills.

The different percentages in pigment concentrations for (a), (b) and (c) will be considered more specifically at later stages but briefly it can be mentioned that in:

(a) The only materials present are the particles of solid and the vehicle;
(b) Milling media (balls or beads of various types) modify the conditions;
(c) The conditions of the whole are further modified because ball mill dispersions are actuated by gravity and may not operate successfully with high viscosities induced by the highest possible pigment concentration.

With respect to (d), although stabilisation has been considered previously, further emphasis of this important stage would not be amiss here. Immediately after the dispersion process is stopped the tendency, as stated, to deteriorate and at an ever-increasing rate is inevitable. Any attempt to stabilise the product once it has been discharged from the mill, will invariably increase the flocculation, because additions of anything, not absolutely identical, to a colloidal dispersion of this nature, has a destabilising effect. Moreover, the rate of flocculation may be increased unless a specific polymer acting as a colloidal protective is present. Therefore it is obviously better to stabilise whenever possible in the mill so that flocculation resulting from the addition of stabilising (or other) component could be remilled satisfactorily by further action.

Stabilisation in the mill can be readily accomplished with the batch mills indicated by (a), (b) and (c) of Fig. 2 although with (c) (ball mills) the procedure is rather more laborious than with (a) and (b). With respect to continuous mills, however, as will be discussed later, there are problems and the most suitable procedure is to ensure that the base being prepared for the continuous mill is stabilised (i.e. brought to a stable formulation by suitable additions) before being presented to the continuous mill.

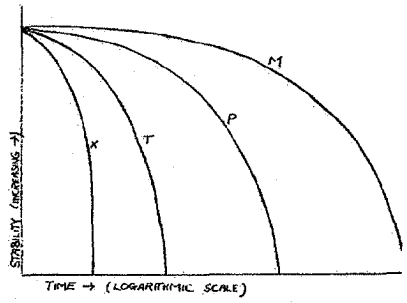


Fig. 3. Stability curves of milled products stabilised at different stages of milling.

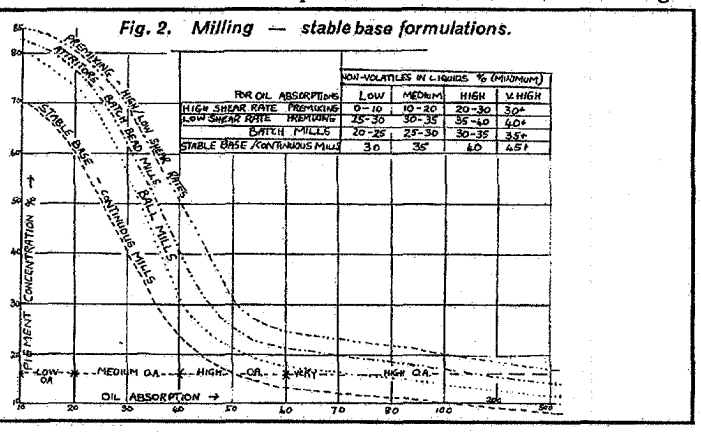
Figure 3 stresses the importance of stabilisation and the stage at which it is carried out. The curves denote the likely results if tests were carried out to check the stability of a milled product stabilised:

(a) In the mill before discharge—thus enabling any floccules formed to be remilled—curve M;
(b) Immediately after discharge (i.e. within minutes)—curve P;
(c) Some time after discharge (e.g. 24 hours)—curve T.

Curve X, on the other hand, denotes the material which has not been stabilised at all.

The curves will invariably be in the same sequence for all combinations of materials but the actual times and intervals will be dependent upon the products.

Fig. 2. Milling — stable base formulations.



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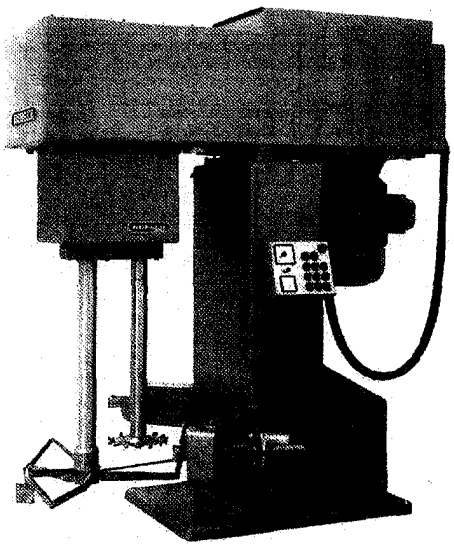

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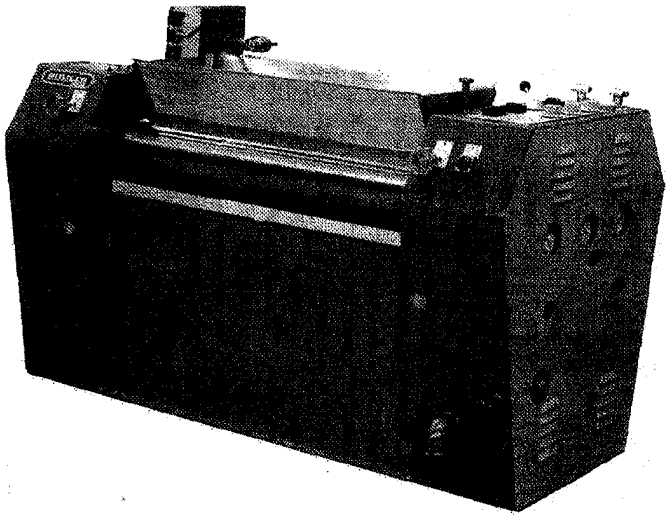

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Rheological considerations

It has been stated that provided the milling formulations adhere to the basic indications in Table 2, the viscosity of the mill bases will generally be satisfactory for the process or require only minor modifications dependent on the equipment. Nevertheless, it is considered that an appreciation of the flow characteristics, both of the raw materials and products, would be helpful. Therefore before assessing the dispersion equipment available, basic rheological phenomena and their effect on dispersion processes will be noted.

General

The basis of determining the resistance of a fluid, to a shearing force under laminar flow conditions, i.e. determination of the viscosity of the fluid, depends initially on the concept of simple flow. Imagine a fluid flowing such that planes are parallel in motion (i.e. the flow is laminar) and the velocity difference between the planes is directly proportional to the distance between them. Then assuming the force causing the flow is tangential we can derive the following:

Shear stress = force per unit area;

Shear rate = differential velocity per differential width;

Viscosity = shear stress per shear rate, i.e. shear stress/shear rate.

Actually the above is more specifically called the *dynamic viscosity* which, if divided by the relative density of the fluid, yields a result called the *kinematic viscosity*.

In terms of the dimensions—length (L), mass (M) and time (T), viscosity may be represented thus:

Dynamic viscosity, $ML^{-1}T^{-1}$

Kinematic viscosity, L^2T^{-1}.

The simple flow concept considered above can, however, only be attributed to fluids exhibiting Newtonian behaviour.

Newtonian viscosity

Newtonian behaviour is exhibited by gases, liquids and solutions of low molecular weight. The viscosity of a Newtonian fluid depends on temperature and pressure and is independent of the rate of shear. The diagram relating the shear stress and shear rate for Newtonian fluids is therefore a straight line through the origin subtending an angle (to the shear rate axis), the tangent of which (μ) is equal to the Newtonian viscosity (Fig. 4).

Low viscosity systems are not satisfactory for efficient dispersion operations. On the other hand high viscosity systems, when possible, would be excellent for this purpose.

Non-newtonian systems

The viscosity of these is dependent on the acting stress and therefore cannot be characterised by one determination.

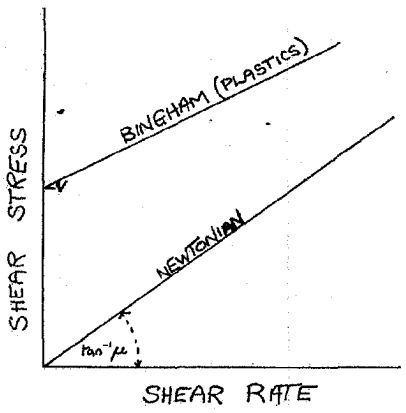


Fig. 4. Flow curves for Newtonian and Bingham (plastic) fluids.

Unfortunately, a single determination on an unsuitable instrument is still often presented for acceptance when several determinations for a graphical evaluation is required.

Non-Newtonian systems may be subdivided:

1. Viscosity independent of duration of stress including
   - Bingham (plasticity);
   - Pseudoplasticity;
   - Dilatancy.
2. Viscosity dependent on duration of stress
   - Thixotropy;
   - False body;
   - Rheopecticity;
   - Rheopexy.
3. Viscosity modified by elasticity, hence viscoelasticity.

The above are discussed in greater detail as follows:

1. Viscosity independent of duration of stress

Bingham plasticity

This is exhibited by some high particle/vehicle ratio dispersions which has a structural rigidity resisting any stress lower than the yield value V (Fig. 4). When this is exceeded the structure breaks down and the whole behaves as a high viscosity Newtonian fluid, rheologically ideal for dispersion operations. When the stress is reduced, the Bingham Plastic may not recover its original shape but it regains its original structure or rigidity. This emphasises the advisability of reduction while operating (cf. False Body).

Pseudoplasticity

This exhibits a progressive fall of "apparent viscosity" (i.e. shear stress ÷ shear rate) with increasing shear stress (Fig. 5). There is no yield value but beyond a given shear stress, further increase results in Newtonian characteristics. Removal of shear stress usually results in reversion to initial state. These systems are not ideal for dispersion exercises because of the reduction in apparent viscosity with increase in shear stress. Organic pigments, if present, may adsorb vehicle to increase the consistency to an acceptable level, however, although it is more likely to occur in the Newtonian range.

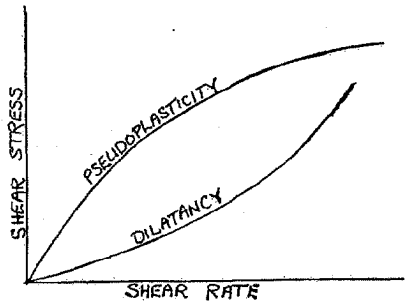


Fig. 5. Flow curves for pseudoplastic and dilatant fluids.

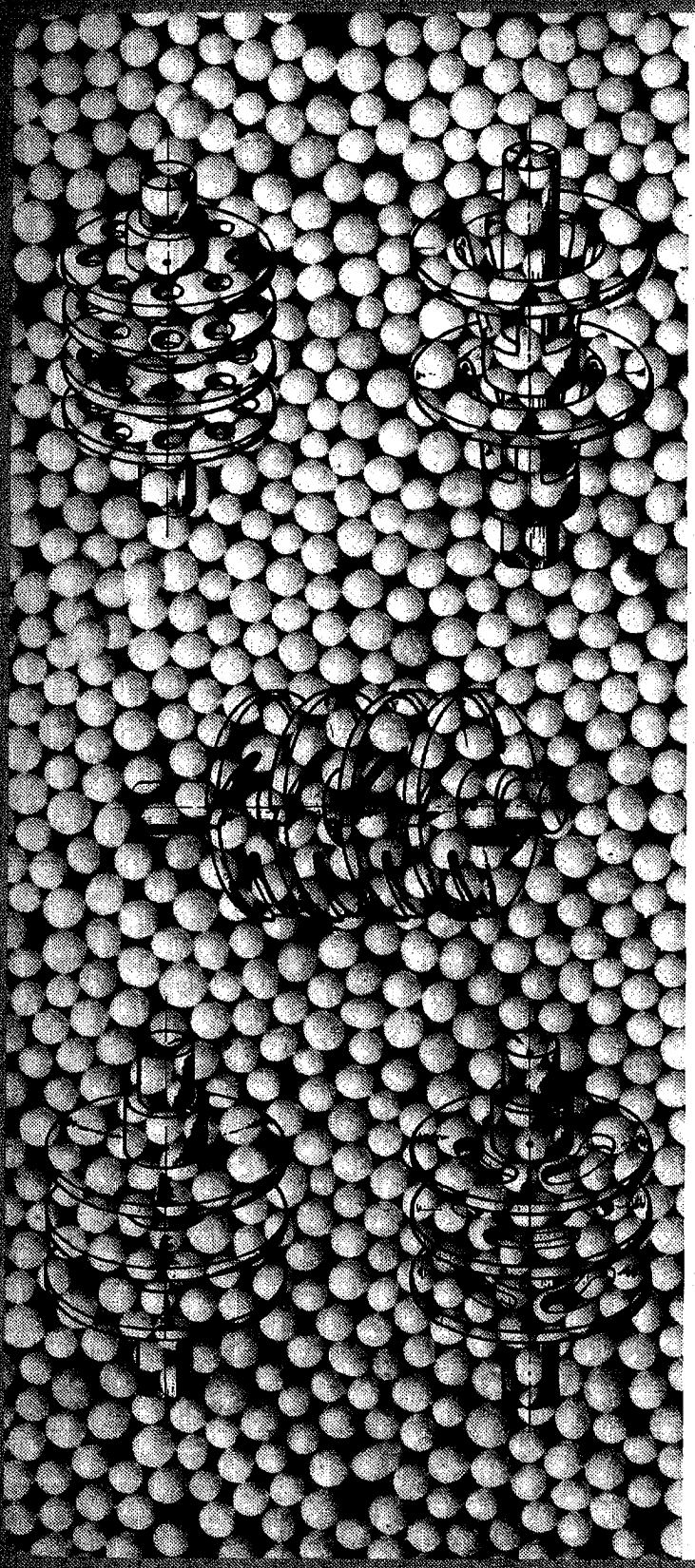
Dilatancy (Fig. 5)

This shows an increase in "apparent viscosity" with increasing stress. There is no yield value and the structure is basically completely deflocculated with only enough liquid to fill the voids of the closely packed particles. Very low shear rates enable lubrication with little stress but at higher rates of stress the dense packing breaks and the material expands or "dilates" with increase in voids. This reduces the available liquid for lubrication and the applied stress has to be much greater. Dilatant systems are not satisfactory for dispersion operations, but when their temperature is increased (from room to say 60°C) they often behave as Bingham Plastics which are ideal for dispersion (e.g. in high-speed disperser/mixers) provided that reduction is effected before the operation is stopped.

2. Viscosity dependent on duration of stress

Thixotropy

This is a reversible time-dependent loss of consistency accompanying the application of shear (or the increase in the amount of applied shear). Structure breaks down with time if sheared at a given rate until an equilibrium is reached. Further breakdown can be induced only by increasing shear rate. All the thixotropy can be sheared out if the shear rate is high enough. A measure of thixotropy or thixotropic breakdown can be gauged from the area of the hysteresis loop in the shear stress/rate graph. The latter is prepared by taking readings when the shear rate is increased to a maximum in predetermined increments and then decreased likewise to zero with the time intervals between readings being constant. The shape of the return curve of the hysteresis loop indicates that thixotropy is a complication superimposed on the other residual states, e.g. Fig. 6 shows:



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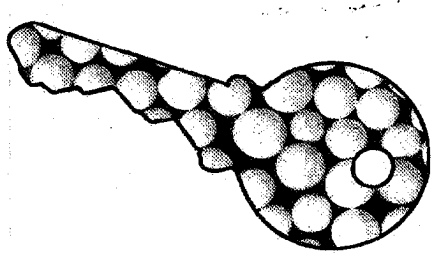

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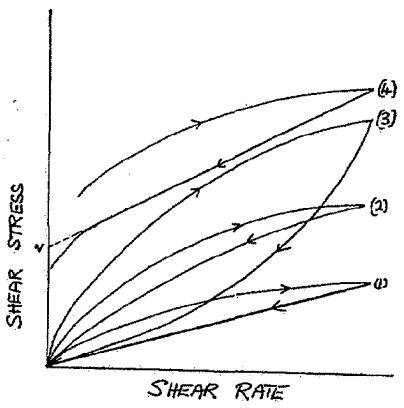

Fig. 6. Flow curves, thixotropic types.

1. Newtonian characteristics;
2. Pseudoplastic behaviour;
3. Dilatant phenomena;
4. Bingham-type features (see False Body).

Thixotropy is not the ideal condition for dispersion operations which, however, may be possible provided that:

(a) The stress has been in action for some time such that stable conditions are obtained and stress will not vary;

(b) The shear stress has been so great that all the thixotropy has been sheared out;

(c) The system is being used on the return of the hysteresis loop showing Bingham or Newtonian characteristics.

In any of the above the viscosity may be rather low for satisfactory dispersion initially. If organic pigments are used, however, continued operations are likely to cause further medium adsorption resulting in increasing consistency.

False body

Indicates thixotropy in Bingham-type Plastic behaviour (Fig. 6, curve 4). True thixotropes breakdown completely under high stresses and behave like true liquids even after the stress ceases until the structure reforms. False-bodied materials do not lose their solid properties entirely and can still exhibit a yield value even though this might be diminished. The original value is regained after resting a long time.

Rheopecticity

A tendency to form a structure on standing accelerated by *gentle* shearing. Excessive shearing action (beyond a critical amount) destroys the structure. This would be the stage for a dispersion process to start but this type of consistency would be better avoided.

Rheopexy

This denotes formation of structure only under shear and disintegration at rest. Rapid or violent shearing though may prevent structure formation but dispersion with this rheological condition would be difficult.

4. Viscoelastic fluids

Such materials are usually very highly viscous fluids. The reversible element (elasticity) cannot be manifest while the irreversible principle (viscous flow) is occurring and changing the shape at the same time. Materials such as doughs are viscoelastic and should dispersion operations be indicated sustained shear stress to overcome the elasticity is required.

Dispersion equipment

The basic principles embodying the most efficient dispersion techniques are constant irrespective of the type of equipment employed. The application of the principles however must show some variation because of the differences inherent in the operation of the varied dispersion plant, as will become apparent when the latter is considered in detail in the following pages.

Dispersion equipment may readily be subdivided into two main classes:

(a) batch mills;

(b) continuous mills.

Each class is capable of further subdivision, while it must be stated that continuous processes could at some given stage be fed with materials which may have been prepared by a batch process. This is noted so that the fact that a "continuous" mill is being used does not necessarily mean that the whole process is continuous.

The major mills representative of the two main classes are:

(a) batch mills—ball mills, attritors, batch bead mills, mixers;

(b) continuous mills—bead/sand mills, roll mills.

All mills must be earthed satisfactorily and precautions taken to avoid static in the charge. One method is to ensure polarity in the milling base.

Batch mills will be considered initially.

Ball mills

Introduction

These mills are horizontally-mounted cylinders partially filled with milling media. Rotation round the axis is designed to cause the media to be raised to a given height and then allowed to cascade under the influence of gravity, to the bottom of the mill. Mill base in the interstices is therefore subjected to a shearing action, provided that laminar flow appertains, thus providing the dispersing action.

"Steel" ball mills, designed to cope with metallic milling media, have a metal liner and the larger types are water cooled. "Pebble" or "porcelain" ball mills have ceramic type liners and cannot readily be water cooled. The milling media for these latter mills are non-metallic.

Ball mills have been the work-horse of the paint and other industries for many years and, because over this period of time reasonable results have usually been obtained without too much worry, a certain laxity in procedure has developed. This has led to unsatisfactory results when dealing with the more sophisticated materials of recent years, although partially the trouble has been the misuse of the mills. Nevertheless many ball mills are still in operation and will continue to do sterling work.

Speed of rotation

The rotational speed must ensure sufficient cascading of the milling media. However, the concept of having a variable speed so that it may be varied with different materials being processed is quite unrealistic. A practical approach to the subject is vital, although much play has been made on an idea of insisting on a specific fraction of the critical speed. However, the variation likely, even during the manufacture of one item, necessitates the compilation of a table (see below) indicating the range of speeds most likely to prove effective. The dispersion practitioner can then determine whether over a period a slight change in speed is advantageous.

TABLE 3. SPEED OF ROTATION FOR BALL MILLS

Ball mill internal diameter feet	Recommended speed of mill range revs per min
1	48-52
2	32-36
3	24-28
4	20-24
5	18-22
6	16-20
7	14-18
8	12-16

Milling media

(a) **Shape.** Three main shapes are available:

(i) **Spheres** are the most logical type of members for ease of cascading within any circumference. Moreover, the smallest uniform interstices make spheres the most efficient shape for milling media.

(ii) **Ovoids** in the natural form of pebbles are the cheapest. There has been, however, a hypnotic compulsion for this shape and synthetic (composition) "natural shape" ovoids have been available. With interstices that are quite irregular ovoids cannot be seriously regarded as efficient as spheres.

(iii) **Cylinders (or rods)** were originally conceived as joining up in the mill to form rollers along the whole length! This situation never occurs and the cylinders are completely randomised in position with totally irregular interstices. The same weight of cylinders would need less base than would spheres or ovoids

in each batch operation. Cylinders must therefore be considered less efficient than ovoids or spheres.

(b) **Size.** The smaller the milling media the more efficient is the dispersion. Figure 7 illustrates the results obtained by milling the identical mixture in (a) a lab ball mill with 12 mm balls, and (b) a lab bead mill using 1.2 mm beads. Although the speed of milling is vastly different (nearly a week for the ball mill; less than an hour for the bead mill), it is obvious the colour development in the ball mill will never equal that in the bead mill. Milling media should therefore be as small as possible, but note:

(i) The smaller the media the more buoyant are the members (because of large surface area) to the paste, reducing the efficiency of cascading.

(i) The smaller the media the more paste is retained on the surface, i.e. it becomes more difficult to empty and clean the mill.

(iii) The media must be big enough to be retained in the ball mill when emptied.

For the best ball mill work media exceeding 15 mm in diameter should be avoided.

(c) **Relative density.** Other factors being equal, the higher the density of the milling media the better is the degree of dispersion in a given time. However, the main advantage of higher density media is the fact that higher viscosities (and therefore higher pigment loading) are possible which definitely enhances the efficiency of dispersion. The density of the media is of course a function of the composition which is discussed below.

(d) **Composition.** The composition of the milling media determines both the density and wear. It is therefore necessary to check details.

Metallic milling media should be through-hardened by heat. It may not be wise to obtain "work hardening" media which may wear too much before work hardening occurs. Metallic media that are not through-hardened will wear rapidly into unsatisfactory shapes. Apart from through-hardened ball-bearings, other media prepared from high nickel or high chrome content steels have been satisfactory.

Non-metallic milling media. The one-time cheapest, i.e. the natural ovoid pebbles, are now almost unobtainable and therefore synthetic types are virtually absolutely necessary. These may be based on steatite, other ceramic types (including porcelain) and alumina. Some of these are described as high density but the description should not be applied unless the relative density is 3.5 minimum, i.e. about 50% in excees of that for the general pebble/ceramic media.

Lab or works scale checks are necessary to check wear, but it can be categorically stated that media prepared by a sintering process should be avoided. These usually exhibit a high rate of wear while contaminating the pigment base with an unwanted extender. Fused media are necessary and even here the variation is such that tests are still recommended. It should be noted that cylinders (or rods) having circular but sharp edges can be rapidly eroded in those areas.

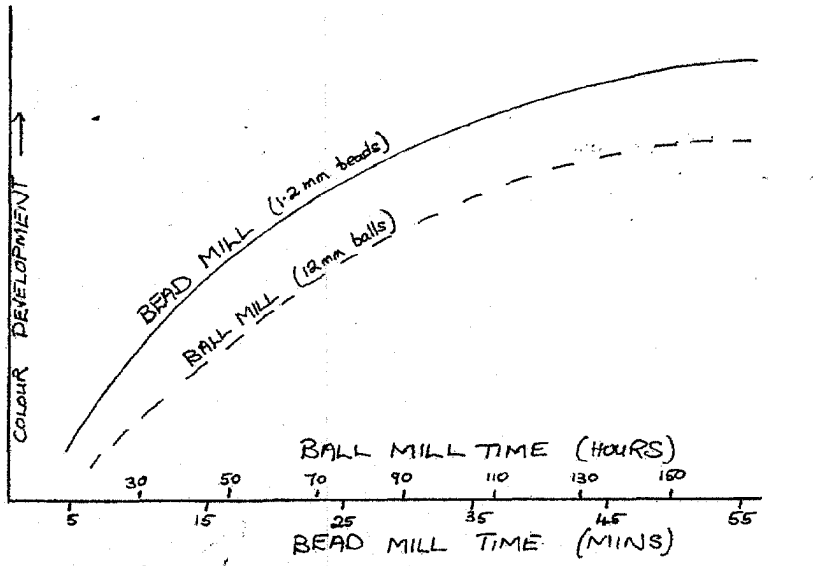

Fig. 7 Effect of milling media size on colour development

(e) **Mill charge**

(i) The mill should be charged with one size of milling media. The practice of having two or more sizes has no real foundation, in fact:

(a) During the milling process the media often partially classify;

(b) If they do not classify but remain well mixed, the interstices are randomised and become larger, reducing the process efficiency.

(ii) Non-metallic media, whether ovoids or spheres, should be charged to approximately half way. However, if using very high density materials, care must be taken to ensure that the liner of the mill will accommodate the pounding due to the high weight. If not it may be wise to reduce the actual charge of media accordingly as is often the case with metallic media. Non-metallic media may often with advantage be loaded into a steel-lined mill.

(iii) Metallic media are invariably loaded into a steel-lined mill, never into a "porcelain" mill. Provided the mill and motor can accommodate the weight of metal, the steel-lined mills are ideally loaded with the metallic media up to half way as for the non-metallic media. However some mills may be worn, underpowered or not designed for the full load. In such cases the more usual loading is 33⅓% apparent volume of the mill.

Note 1

Mills which have smooth sides (steel mills) or which have very high density media, or which are charged only partially with media (rather than full 50% charge) may be provided with "lifter bars" to help raise the media to the cascading position. This is invariably the case with steel mills (except the smallest and lab mills) and sometimes the position with the larger "porcelain" mills.

Note 2

In order to calculate the charge by weight when the relative density is known the following may be used:

Spheres will have a void volume of about 35% of total apparent volume;

Ovoids will have a void volume of about 40% of total apparent volume;

Cylinders will have a void volume of about 30% of total apparent volume.

Pigment mill base charge

The composition of this should adhere as closely as possible to the guide lines in Table 2 or the relevant ball mill curve in Fig. 2. The volume of the base should fill the voids of the milling media while operating, i.e. as the voids will effectively be slightly greater than the values given in Note 2 above, the volume of the base would be as determined as follows:

With spheres 40% of the total apparent volume of media;

With ovoids 45% of the total apparent volume of media;

With cylinders (or rods) 35% of the total apparent volume of media.

The total apparent volume of the media of course is the total volume of the actual media and the voids. This means that if the total apparent volume of the milling media is 50% of the total empty volume of the mill, the volume of mill base expressed as a percentage of the total mill volume would be:

for spheres 20%;
for ovoids 22.5%;
for cylinders 17.5%.

The latitude in each case would be

± 2.5%. It must be noted of course that if the apparent volume of media is less than 50% the above figures are reduced accordingly; for example some steel mills would be loaded only with an equivalent of 33⅓% of the total empty mill volume which would mean reducing the figures to 66⅔% of those for 50% apparent loading. Overcharging the mill with mill base reduces the efficiency of milling while undercharging increases milling (or dispersing) efficiency but increases the wear of mill and milling media with consequent added possibility of contamination.

After some use any wear should be noted and, if there is a delay in making up any loss with new media, a reduced volume of mill base should be used, otherwise inefficient milling results.

Milling procedure

Once the mill base formulation has been established and the requisite volume (suitable for the milling media) determined the dispersion exercise can be started. Liquids are loaded initially but a portion is retained to wash in the solid pigments. If a non-metal liner mill is used a polar material if possible should be in all portions loaded, into the open mill, to avoid or reduce static build-up. When all the additions are made the mill is clamped down and allowed to rotate. Of course the whole mill base may be premixed before charging.

The first couple of hours is purely a mixing action (unless the whole was premixed) to distribute the solids and liquids as evenly as possible to enable dispersion to occur. It is necessary, however, to determine whether cascading is occurring or whether by some mischance the consistency has been too great for satisfactory milling. This may be due to either a new material which has not been evaluated or a batch of material which has been prepared with a higher viscosity or oil absorption than usual.

On the basis that it is easier to reduce rather than increase the viscosity of a batch in a mill there is a slight bias in the figures derived from the curve which would make the base have this bias. Mostly there is no need to make any modification, but should slight thinning be desirable solvent or solvent/resin solution should be used just to cause the change required. Many high oil absorption pigments cause undue and regular thickening with high yield points and thixotropy. The addition of resin at a number of stages is usually called for here. Whatever additions are made should be as little as possible, i.e. just enough to enable flow even if this procedure has to be repeated a number of times; in this way a better dispersion is possible than if the total, finally added, would have been added initially.

This procedure is not very popular because of the labour involved in opening the ball mill, adding the resin, etc., closing the mill and restarting. For this reason, unless the most critical results are required, there is a tendency to add more liquid than necessary to make the base just to flow, to avoid further additions.

Milling times

If milling times exceed the "norm", then, unless specific conditions have caused the problem and can readily be identified, the formulation and quantity of base must be checked together with the milling media size and quantity.

If first-class dispersion of organic pigments is required the results should be achieved within 48 hours. Only very exceptionally difficult pigments would require 72 hours. Apart from these two times most materials should be readily milled within 24 hours or less.

Stabilisation

When the dispersion is completed stabilisation is necessary by adding resin, etc., to bring the formulation to that suggested in Table 1. The number of resin additions and consequent rotations (to remill any flocculation) depends on the non-volatiles of the resin in the pigment base as shown in Table 4 below.

TABLE 4

Non-volatiles of resin in pigment base %	Number of additions of resin solution for stabilisation
40+	1
30+	2
25+	3 (with care 2 possible)
20+	4 (with care 3 possible)
15+	5 (with care 4 possible)

Where a large number of additions is necessary, a small quantity of resin should be added at first and the quantity increased with each addition. It is necessary to rotate the mill after each addition for half to one hour in order to remill any flocculation. If at any one time the flocculation persists, then resin solution has not been added in sufficiently small quantities.

Attritors

These machines are vertically standing cylinders filled to a certain height with milling media which are moved by a number of rods attached to a central rotating shaft actuated by an electric motor. The shell of the cylinder, which is usually hardened steel, does not rotate. The milling media, which can be either metallic or non-metallic, are preferably approx. ¼in. spheres. U.K. suppliers (Torrance & Sons Ltd) have at one time advocated a mixture of ¼in. and ⅛in. spheres but the writer considers that the reasons for this recommendation are not valid.

It is of course the prerogative of the dispersion practitioner to decide on the size, shape and composition of the milling media and indeed ⅛in. diameter metallic spheres have been advocated for special purposes (in modified machines). The usual type of Attritor has facilities for water cooling but special models, such as with ceramic shells, may prove unrealistic in this respect. The suppliers have introduced a new type of Attritor (designated Q) suitable for large batches which will be discussed at a later stage. The original (S type) is considered first.

The S type machines may be charged at the top and emptied at the bottom, the media being retained by a screen. However, the larger sizes are usually provided with a circulating device, usually an advisable adjunct to avoid sluggish or dead spots, which does enable an alternative position for discharge.

The Attritor is a very versatile machine, although it is a batch processor, and it is possible to vary the milling media content very easily if desired. However, formulations for the full load are advised in order to avoid hold-ups and possible errors.

The composition of the milling media may be similar to that described in the section on ball mills. Once again it is emphasised that sintered media are not advisable. The quantity is that required just to cover the top impeller rod. Metallic media are used for those materials containing a fair quantity of black pigment, while non-metallic media would be used for "clean" colours. However, it is doubtful whether one can obtain results as clean as obtainable from a "porcelain" ball mill with non-metallic media unless the Attritor is likewise lined with non-metallic (i.e. ceramic type) material.

For the best results the pigment mill base must not exceed in volume, that of the voids of the milling media in motion. Once again this volume can be taken to be approximately 40% of the total apparent volume of the milling media (i.e. the metal and the voids). If this figure of 40% is substantially exceeded, the final result will certainly take longer to achieve and may even be not up to the standard required no matter how long the milling proceeds.

The composition of the pigment mill base should be based on the suggestions in Table II and also on the Attritor curve given in Fig. II. This will ensure that the consistency is satisfactory for the flow to be laminar, thus enabling adequate shearing action.

Charging methods

There are basically two methods of charging the Attritor with the pigment mill base.

(1) Some of the liquids are charged, the Attritor is started and the solids added. The remainder of the liquids is

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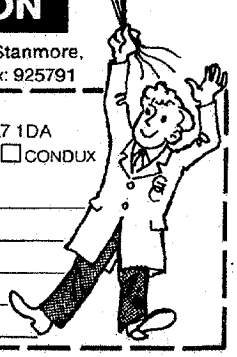

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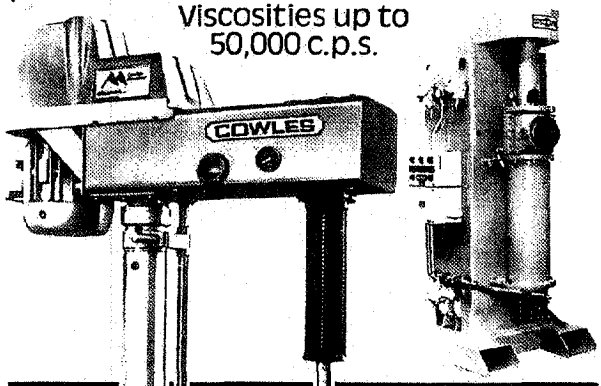

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used to wash in the solids while the machine is operating. This is a very suitable method provided that "dusty" materials are avoided or are sufficiently carefully added to prevent contamination of other plant, or parts of the Attritor, difficult to clean.

(2) The whole milling formulation is premixed and then added to the Attritor either by pumping or preferably via a chute. This method is to be preferred especially for the larger machines and also when several batches of the same material are required. In the latter case a very large premixed milling base is prepared and milled in succession in the requisite quantities.

Stabilisation

When the required dispersion has been obtained, stabilisation is necessary as with the other batch mills. In this case the procedure offers less problems because, compared with a ball mill, the Attritor is an "open" mill. In other words, the stabilising liquid is added to the top of the mill while the machine is operating. This is a great advantage, not only because the labour-intensive method of ball mill stabilisation is avoided, but the liquid is incorporated as added and does not remain on the surface of the original pigment base as it must do for some time in ball mills. Initially the liquid should be added slowly—ideally at a rate not exceeding the rate of incorporation. As this occurs incorporation becomes easier and faster, enabling the rate of addition to be increased until the "stable" formula as recommended in Table I. The mill is then discharged and cleaned out with the remaining liquids in the formulation or another fraction of the same type added for milling.

Comparisons with ball mills

It has been claimed that the Attritor is about ten times as fast as a ball mill. Broadly speaking this is correct. The reasons for this faster milling can be deduced as follows:

(a) The Attritor is actuated by means of an electric motor which rotates the milling media. The media in a ball mill is caused to cascade by means of gravity. If the viscosity tends to reduce the cascading efficiency in the ball mill there will be less efficient milling. In the Attritor however a higher viscosity (and therefore higher pigmentation and more efficient dispersion) is tolerated.

(b) The milling media in an Attritor is smaller than in the conventional ball mill. Reference has been made previously to the improved milling associated with the reduction in size of the milling media and exactly the same argument holds. Smaller media means smaller interstices with greater control for laminer flow.

(c) When operating the Attritor most of the separate members of the milling media are in motion. With ball mills, however, a large proportion of the media at any one time may be quite motionless or be moving very slightly until they reach the position in the mill when they start to cascade. The larger the mill, the larger the volume of media affected by the conditions noted above.

It must be remembered, however, when comparing times of milling, that the ball mill is usually allowed to operate unattended overnight because it is an enclosed type of machine. The Attritor, if operation for fractions of a day is necessary, must be attended for the full time unless arrangements are made for an extended day or left running with full safety devices. This may not be popular, especially these days, and the time saved may not be worth all the safety and other factors. Therefore if it is realistic to assume that "S" type Attritors are likely to run for the eight-hour customary day, then the factor of ten times faster than the ball mill must be reduced to three or four times faster. Of course, if an extended day is run the factor will be increased.

Most materials that are processed on ball mills are readily made on Attritors, those requiring steel ball mills usually being processed with metallic media as would be expected. There are, however, some examples where transfer from ball mill to Attritor manufacture may present some difficulty.

Some examples are:

(a) Some materials are required to have an exceptional cleanliness which can only be obtained from a pebble or porcelain ball mill with non-metallic media. Such products would require the Attritor to be wholly constructed or lined with a ceramic type of material. This may be costly or difficult to operate.

(b) Some products have specific organic extenders which are hammered by the balls in a ball mill to give a specific fairly repeatable required pattern. Although this is strictly not a dispersion problem, it may present quite some difficulties to transfer from a ball mill to an Attritor.

The Q type Attritor is basically a modified S type which is connected to a high-speed mixer/disperser (which will be discussed at a later stage) such that the mix, i.e. the pigment mill base, is circulated continuously between the Attritor and the disperser, by means of a pump and other connections, while both machines are operating.

The high-speed mixer disperser is of a greater capacity than the Attritor, allowing a batch of material up to ten times that normally made by the same size S model. The claim for the Q model is that the total time for manufacture (e.g. for making the batch 10 times that of the usual "S" size) is much less than the manufacture of the (ten) single batches, sometimes saving up to 40% of the time.

There is some substance in this claim, but the time saved varies considerably, dependent on:

(1) The formulation;

(2) The size of the original S machines, some of which are modified differently to make them more efficient, e.g. with more media and the addition of a grinding surface-cum-strainer.

Nevertheless it is an interesting machine for larger batches, especially for bulk primer and surface manufacture.

Batch bead mills

These machines in their simplest form are like the Attritor, being vertical cylinders in which the media are rotated, the shell remaining fixed. The original Berger-designed mill grew from a simple design sketched in Fig. 8 and some relevant details are as follows:

Milling media—these were originally glass beads 1.2-1.5mm in diameter. The quantity of milling media was approx. 0.5 kg/per litre total empty volume of the mill. Thus the apparent volume of milling media was less than 30% of the total empty capacity of the mill shell.

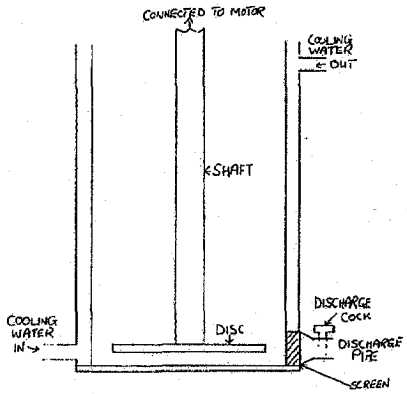

Fig. 8 Simple batch bead mill.

Power—for adequate power minimum of 1 kW for every 10 kg milling media is suggested.

Disc—the size of the disc positioned to aid discharge must be adequate to cause all the milling media to be sufficiently well rotated when the machine is in operation. Although a figure of 80% of the mill diameter is suggested to be a reasonable diameter for the disc, it must be remembered that scaling up (or down) changes the distance from the disc edge to the tank (shell) side. If this distance is too large slip may occur which will reduce efficiency. The smallest laboratory-type machine will operate successfully with plain discs. Larger machines have either modified types of impeller discs or have holes in the discs to enable the milling media to be actuated easily. The peripheral speed of the disc is of the

order of 750 m/min. for general purposes. It should be noted, however, that if for some reason higher speeds are desirable, there would be a limitation imposed upon the size of glass milling media; e.g. glass beads of 3mm in diameter would tend to shatter at speeds exceeding the figure noted above. The disc of course should be manufactured from hardened or chromium-plated steel.

Method of operation

The batch bead mill, with smaller milling media and faster rotation, disperses at a faster rate than the Attritor. However, if very coarse pigments or extenders are used, the glass milling media may wear quite rapidly. There is of course the possibility of using different composition beads, but here again caution is advised and sintered media should not be considered.

The composition of the pigment mill base must be prepared in accordance with Table II or the relevant curve in Fig. II and the methods of charging would be similar to that suggested for Attritors, that is:

(a) Add some liquids, start operating, add solids and wash in with remaining liquids;

(b) Prepare the pigment mill base as a premix and add the whole to the beads in the mill.

As with other mills, the volume of mill base should be equal to the void volume while operating to obtain the most efficient dispersing action. Mill times vary with the raw materials e.g. up to 15 min. for readily dispersable materials, 30-40 min. for most organic pigments and 60 min. for blacks.

These times are exceeded only when abnormally difficult products are processed, e.g. transparent oxides. When the milling is satisfactory, stabilisation is accomplished, bringing the formulation to that of Table I, in a manner similar to that described for Attritors.

If the simple type shown in Fig. 8 is used, there is a tendency for some inadequately milled paste to accumulate in the region between the screen and discharge valve. Therefore, when the milling is virtually completed, some of the milled base is discharged and recharged at the top to wash out the poorly milled base back into the mill for adequate milling while a similar procedure is adopted during the early stages of stabilisation. Alternatively a circulation system can be used.

This procedure is, however, unnecessary in the modification introduced by Torrance (who supply this type of machine), by having a precision-built valve fitting into the screen—discharge region which does not allow build-up to occur. Apart from the modified types supplied by Torrance, it must be mentioned that other types of batch bead mills have been available that are different from the simple type in many respects, but mainly from an operational point of view, in having a method of discharge based on centrifugal action. These mills, of which the Centrimill (OBS Machines) and Monomill (August) are examples, are treated in the usual way for the best procedure, i.e. the pigment mill base must be equivalent to the void volume when operating (i.e. about 40% of the total apparent volume of the media and voids). With a lower peripheral speed some suppliers advocate the use of 3mm beads for their models.

A final point to bear in mind is when charging or changing media. Some suppliers have been known to switch to different manufacturers of glass, with the result that sometimes leaded glass and at other times non-leaded glass is available. If charging is by weight the relative density should be carefully checked every time, to determine required volume. The rate of wear of glass media has not indicated a wide variation between grades of glass. It will, however, be found that the rate of wear varies inversely as the diameter of the media; therefore the choice of 2mm media may be wise from an economic point of view.

Mixers and mixing

I Introduction

The usual objective of mixing is homogenisation, shown by a reduction of concentration or temperature gradients or of both simultaneously. Of course the degree of homogenisation depends on the end use. Thus the criteria determining the suitability of a cement mix cannot be used when assessing homoeopathic doses. In a like manner the degree of homogenisation of a particulate solid mixed into a liquid may be quite different from that of a dispersion of that same solid/liquid system.

Although the mixing process is used so widely and has been studied comprehensively, the design of mixers for specific processes is fraught with difficulties. The most successful approach is to base the design on a mixer used in a similar process, but if one is not available it is always better to err on the side of higher available power and stronger construction, even when using specific formulations issued for guidance.

II Mixers for dispersion

Although it is the case that when mixers are used as dispersers it is often implied that specific types of mixers are used, it must be remembered that it is the formulation being processed that determines to a great extent the success or otherwise of the operation. It is necessary to emphasise this so that a flexibility in approach is possible with respect to the use of available plant. This, of course, is in line with the oft-repeated precept that dispersion necessitates laminar flow, to accomplish which requires high viscosity, a function of the basic mill formulation.

It is best to consider two extreme designs of mixers and to relate others to these extremes or regard them as intermediates. The basic two types are: (a) high shear stress—which are low shear rate types, and (b) low shear stress—which are high shear rate types often called high speed mixers or high speed dispersers.

III High shear stress (low shear rate) mixers

Many different models of this type of mixer are available and the materials of construction are important because they are basically heavy duty machines. An idea of the wide variation can be obtained by comparing the ratios of power supplied to capacity of the working compartment. The latter can vary from a small heavily constructed cell to large change pans.

In some sectors of the rubber/plastics industries and even in the pigment chip industry, when these machines are used the power to base volume ratio can be as great as 2-3 kW per litre. On the other hand in the paint industry the ratio is often no greater than 0.1-0.15 kW per litre. The enormous difference in requirements in the strength of materials of construction can be appreciated.

Basically there are two major types of heavy duty mixers:

(a) *Horizontal* in which the axis of rotation of the impellers is horizontal.

(b) *Vertical* in which the axis is vertical. The advantage of these vertical types however is that they can readily be operated with a change pan system which enables the introduction of a scraper blade as an adjunct to the impeller complex, increasing the efficiency of operation and ease of cleaning.

The numbers of different types of impellers are very great and the construction so varied that it is advisable to discuss the operation from the point of a fully powered well constructed machine (for the paint industry) and if a less well constructed machine is used modification by reduction of viscosity with more liquid would be apposite.

Method of operating

Both machines (the vertical and horizontal) will be treated similarly and provided that the basic techniques of dispersion are adhered to the results will be as expected. Initially the working capacities must be determined:

(a) The quantity of the premixing pigment base,

(b) The total quantity of the stabilised base.

The figure for (b) will determine the total possible working volume as well as fixing the maximum quantity for (a)

which may be further restricted by the power available. The latter may not be sufficient for the high consistency preferred with the high volume wanted. In that case it is better technically to reduce the volume and ensure the consistency.

The object in using a machine of this type can be either:

(i) to premix a pigment mill base for one of the continuous machines, or

(ii) to fully mill the pigment base to its required degree of dispersion such that on stabilisation the base will be usable without further milling.

Whether it is for the first or second reason, it is always advisable to operate in the best procedure possible. It is false, both technically and economically, to consider that as the degree of dispersion required is not so critical, a slap-happy procedure is satisfactory. The latter is more likely to lead to a randomised and probably unsatisfactory result which may not even be repeatable. The only practical way is to proceed strictly as for the best procedure and then stop at the required stage.

Most of the liquids, based on the recommendations from Table II or the premixing curve Fig. II, are charged and the machine started. Cooling may be necessary with some formulations as the pigment or other solid is added and incorporated. Initially the rate of addition is fast, but this is slowed to match the rate of incorporation. The power must be noted to avoid cut-out and liquid added if necessary. Finally if the procedure and formulation have been satisfactory the solids will have just been incorporated with the aid of the residual liquids while the power requirements would indicate the maximum available.

At this stage, as the machine continues to operate to disperse the particulate solid (or pigment), a difference in behaviour (and therefore a necessary difference in procedure) occurs dependent on the material used as described below:

1. If a low oil absorption pigment is being dispersed there is unlikely to be any great change in viscosity which would vary mainly with temperature. As however the temperature had been increasing during the first stage of pigment addition, due to the increase in internal friction, it would have virtually reached a maximum by the time all had been added. Moreover cooling is usually proceeding. The only reduction in viscosity may be due to the retention in the interstices of pigment clusters of extra media which is then released. This is most unlikely to occur in the conditions appertaining but could be matched by unwetted internal surfaces absorbing this released material.

The dispersing action is therefore allowed to proceed for about 15 min., after which time no further perceptible improvement in dispersion would be likely to occur. Therefore stabilisation is effected by allowing the machine to continue to operate while the stabilising liquid is allowed to run into the mixer. This should be slow at least at first, ideally at a rate at which the liquid is being absorbed into the charge. This reduces the tendency to form an interface for any pronounced length of time, and as flocculation always occurs at the interface this procedure is an obvious further safety factor.

If the pigment used was an easily dispersing material, such as most of the titanium dioxide pigments available, it would be quite feasible that the pigment has been sufficiently well dispersed to satisfy even the most critical requirements (e.g. the automotive industry) and the stabilised pigment base would then be suitable for completion to the final paint without further milling. If, on the other hand, the pigment was not an easily dispersible type and required further processing, the stabilised base would be suitable for presenting to the continuous mill for further processing. In the latter case the continuous mill would yield the best possible dispersion only if the premixing had been accomplished in the specific manner prescribed. Indeed, it can be determined at any time that the dispersion of the finally milled material is dependent on the efficiency of the premixing.

2. If a high oil absorption pigment is being processed there is every likelihood of the viscosity increasing because such materials have small sized particles, which when subject to dispersion processes manifest large surface areas *in toto* which have to be wetted by absorption of the liquid. The removal of liquid for the wetting of the surfaces reduces the amount remaining for lubrication and flow. Eventually the consistency may become too great for the machine to operate, in which case further liquid must be added to maintain the operation. Here again only sufficient liquid must be added just to maintain flow (while avoiding motor cut-out or machine distortion) even if this addition is necessary at repeated intervals. This procedure is necessary to avoid reducing the viscosity to such an extent at any stage that very little shear stress is apparent.

Eventually, however, the continued addition is such that the concentration of pigment becomes too low and even the very high consistency maintained will not provide any satisfactory level of shear stress. At this stage therefore the material is brought to a stable type of formulation and presented to another mill for more efficient milling, unless the dispersion is satisfactory. The mill to which the premixed paste is transferred is either one of the continuous sand mill types or the roll mill family.

At this stage is would be helpful to discuss the main reasons why a higher non-volatile vehicle is suggested for the premixing process in a heavy duty mixer (i.e. low shear rate/high shear stress machine) than is recommended for a high speed mixer (to be discussed next).

In point of fact the dispersing action during premixing is equally successfully accomplished in both types of mixers. However, it is in the stabilisation of the premix that trouble may occur.

Firstly it has been emphasised that flocculation readily arises at the interface between dissimilar materials (e.g. a pigmented vehicle and the same vehicle not pigmented). The longer the interface lasts the more time there is for flocculation to occur and last! The slow deliberate mixing of the heavy duty machine tends to create the conditions to favour this unless added at a very slow rate initially as stated.

Secondly, however, the addition of a resin to a pigmented resin with similar non-volatiles will not reduce the overall consistency as markedly as adding the resin to a pigmented low non-volatile resin. In the latter case the consistency will soon reduce to a stage where shearing action is poor, so any flocculation formed has little chance of reincorporation by dispersion action. In the first case of resin addition, however, the reduction in consistency is not so marked and would therefore be sufficient to permit the redispersion readily.

IV High shear rate (low shear stress) mixers

There are numerous types of these, and although some differences can be pronounced they can all be grouped and discussed as High Speed Mixers (or High Speed Dispersers).

The basic mixer is fundamentally a horizontal disc at the bottom of a vertical shaft such that the disc is at a given height above the bottom of the tank. There are many variations:

The disc may have a serrated edge or have holes or added members to increase turbulence at speed, which is usually accepted as a parameter of the periphery. The disc may also be only part of an assembly of a rotor and stator and the speeds may be fixed or two-speed, three-speed or variable either over a given range or infinitely variable to a given speed.

The shaft may be at the centre of the tank or may be movable towards an eccentric position and may be fixed or movable up and down.

The tank may be fitted with an operating scraper and may be fixed or mobile with or without water cooling. It would be most unusual if the tank were not a vertical cylinder.

Much that has been written about the high speed mixer would belong to the realms of mythology. For example, one author claimed that a serrated edge disc

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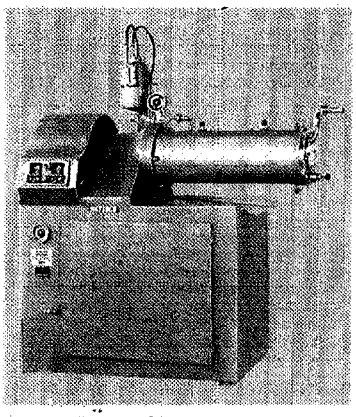

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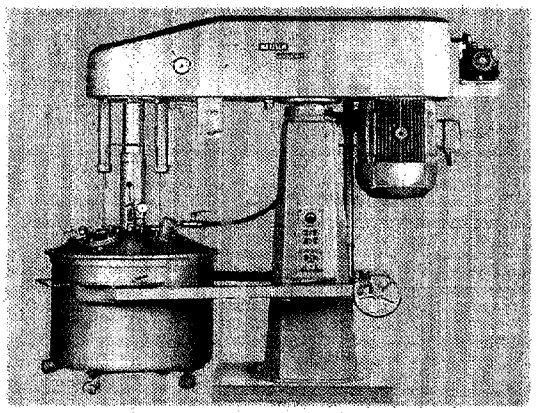

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was unnecessary and that a smooth cylinder was suitable. This would be the case for one particular material at one particular temperature to ensure one particular viscosity. As soon as anything changed, even only minutely fractionally, the whole concept would be proven incorrect!

In the following we will consider the simple high speed mixer and relate to the more complicated variants.

General considerations

A general idea of the parameters involved can be appreciated by examining what has been accepted or promoted as average, e.g.:

Impeller (disc) diameter	= D
Tank diameter	= 2½D ± D
Depth of mix	= 2D – 2½D
Height of impeller above bottom	= ½D – 1D
Peripheral speed of disc for dispersion	= 23 m/sec.

The above may be discussed in dettail:

(a) *Ratio of tank diameter to disc diameter.* It will be recalled that if one starts with a laboratory mixer the ratio of 2½-1 tank-to-disc diameter means that the distance between the edge of the disc and the side of the tank is only an inch or two. When scaling up, the same defined distance becomes a foot or two. This means that the shearing action of the disc periphery is damped down considerably in the large plant compared with the lab. plant. It will be found that sometimes very little motion is observed round the sides of the large tank, whereas with the same formulation the mobility was more than adequate in the lab. Therefore one of three changes may have to be made.

1. The formulation will have to be reduced in viscosity for factory processing. This will reduce the efficiency of premixing—at the very least, will increase the time required for premixing, or may not even result in a satisfactory premix, however long the operation,

2. The peripheral speed should be increased. This will in the first case prove very expensive because the power requirement varies as the square of the speed. Moreover, there would be very little improvement in overcoming the damping effect of the liquid.

3. Increasing the size of the disc relative to the tank. This procedure does make a profound difference even if the peripheral speed is constant. This factor was very evident when easily dispersible organic pigments were first introduced. The original trials on a lab. mill were excellent but poor results followed on the large scale. It was then agreed that the ratio of discs to tank should have been nearer the ratio 1-1½ than 1-2½ when transferred to production size.

From the above it is obvious that dispersion efficiency is dependent on the ratio of disc to tank and the greater this ratio (disc to tank) the more efficient the operation. On the other hand, this procedure of increasing disc size is also expensive, firstly because the power is a function of the cube of the disc diameter, and secondly, if the tank is shrunk (rather than increasing disc size), smaller and maybe uneconomic size batches would result.

Before leaving this section it could be stated that when easily dispersed pigment, such as certain titanium dioxides, a low ratio of disc to tank such as 1-3½ and even 1-nearly 4 has given good results.

(b) *Depth of mix.* It is unlikely that the depth of mix should be any greater than that given. Indeed, if very high consistency mixes are processed it may be necessary to reduce that depth to maintain satisfactory movement for processing to critical requirements.

(c) *Height of impeller above bottom of tank.* If the shaft can be raised and lowered the ideal can be adjusted for each trial. On the other hand, if the whole is fixed, the position of the disc must be arranged so that it is not too high for the initial liquid charge and not too low for effective operation when fully charged. Some basic formulations to be processed should be studied before designing the plant.

(d) *Peripheral speed.* Usually the higher the peripheral speed the better the dispersion because the greater turbulence thus induced can be treated with more pigment to reduce the turbulence by increasing viscosity, creating the conditions for laminar flow. However, the writer has dispersed certain titanium dioxides, specifically designed to disperse easily, at a peripheral speed of 12 m/sec in a tank about 3.75 times the disc diameter. This fact is mentioned because it is emphasised that nothing should be regarded as fixed absolutely—the principles should be known and used in a flexible manner.

Main functions

As with other mixers, the main functions of the high speed mixer with respect to dispersion operations are mainly two-fold:

(a) As a premixer, i.e. to prepare a mill base formulation for subsequent milling in another (usually continuous) mill;

(b) As a premixer/mill combined, i.e. to accept the raw materials and process them sufficiently well that they can be used without further milling for completion to the required product.

Once again it is emphasised that with respect to (a) and (b) above, whether the mill is being used as the final (or only) mill or whether it is being used to prepare material for another mill, the same procedure and care must be applied otherwise the second mill may suffer undue wear or may even not produce the required quality. It cannot be repeated often enough that the premixing is generally the most important part of the whole dispersion process.

Other functions of the high speed mixer include:

(i) Mixing, of course, when the turbulence is allowed full sway. Thus dissolving resins in solvents, pigment chips into resin solutions would be apposite.

(ii) Heating small batches (usually in mobile tanks) for specific purposes:
   (1) When colour matching certain products the colour is "fixed", i.e. not flocculated when the temperature is maintained at 60°C or above for a given time;
   (2) When using specific thickeners based on castor oil derivatives, they have to be incorporated at elevated temperatures, dependent on the composition of the product processed, for required results.

Procedure for premixing or dispersing

The premixing or mill base formulation is determined by referring to Table 2 or the curve for premixing in Fig. 2. The liquids are charged into the tank of the mixer and should cover the disc reasonably well. The mixer is started. If of variable speed, a low speed should be used initially. The pigment or other particulate solid is charged while operating. Increasing speed will be necessary to incorporate the pigment at a satisfactory rate. Incorporation could be helped if the discs can be raised and lowered while operating and also if some of the liquids had been retained to wash in the last of the solids, since the last portions are always more sluggish to incorporate.

Once the stage has been reached when all the particulate solid has been incorporated it is often advisable to scrape down the sides of the tank to incorporate any powder that has settled there. An alternative procedure is to wash the sides down with the minimum quantity of solvent possible, which should have been omitted from the initial charging for this purpose.

The mill will then be allowed to run for about 15-20 minutes, after which time, provided that the charging has been satisfactory, no further real change is likely to occur with respect to the dispersion of the particulate solid. Care must be taken that the mixer is operating satisfactorily, i.e .a "doughnut roll" is evident in the mix with adequate movement round the sides. If these features are absent the formulation being

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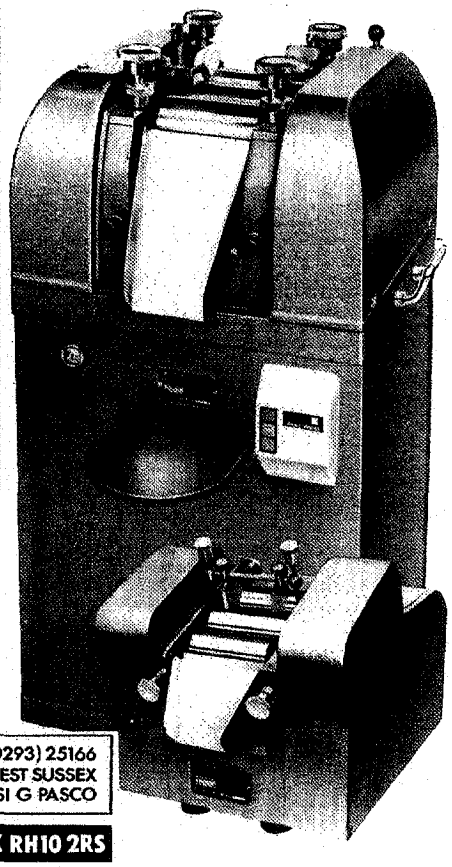

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presented to the mill is inadequate and should be modified either to increase or decrease the consistency.

As with the heavy duty mixers discussed previously, viscosity may increase when processing organic pigments or other high oil absorption solids. Again the minimum quantity of liquids should be added to maintain flow. Even if frequent additions are necessary this is better than a larger single addition for dispersion efficiency.

It will be noted that the mix rapidly becomes heated because of the internal friction. Theoretically the heat should reduce viscosity. In actual fact this is so, but with the high oil absorption pigments the small particle sizes present large surface areas to be wetted and therefore cause a reduction in the resin or other medium available to enable flow. Moreover, the rate of wetting is increased at elevated temperatures. With low oil absorption pigments, however, the particle sizes are much larger and therefore the surface area to be wetted is not so great. Here the elevated temperature would tend to reduce the consistency.

This is made use of in simple formulations including an easily dispersible titanium dioxide, resin solution, an additive such as soya lecithin and white spirit. The titanium dioxide is dispersed in the white spirit and soya lecithin only (hence zero resin non-volatiles quoted in the table) to the extent that the mix may contain up to 80% titanium dioxide! This would normally be a highly dilatant mix, but because the temperature rises in the operation to nearly 70°C the resin on expansion causes a vast reduction in consistency and becomes virtually Newtonian in character. Of course the viscosity is still quite high, enabling the dispersion process to occur. It is imperative, however, that the mixer should not be stopped before full stabilisai on is effected, otherwise cooling will cause the dilatancy to be re-established and it will be impossible to restart the mixer.

Stabilisation should be effected in the usual manner, i.e. by adding the requisite resin solution while the mixer is operating. The addition should be slow at first, to reduce any effect of interfacial reaction, but as the consistency is reduced, the rate of addition may be increased.

It may be pointed out that the liquid non-volatiles for the high speed premixing of low oil absorption pigments is quite low (and even zero, as pointed out above). This is because the low viscosity liquids (solvents and highly solvated resins) are better wetters than the more viscous high solids materials and usually contribute to producing a well-wetted, well-dispersed product. However, at one stage the introduction of new grades of titanium dioxide specifically designed for ease of wetting produced rather unexpected problems. The excellent wetting characteristics caused the titanium dioxide to absorb the low viscosity liquid with such rapidity that pellets were formed enclosing quantities of titanium dioxide that were not available for dispersion because the pellets themselves would not disperse in a high speed mixer and often blocked the entry screen or valve of continuous sand mills.

The procedure adopted to overcome this problem was to ensure the dispersion of the titanium dioxide before it was well wetted. This entailed the use of a high non-volatiles liquid which did not wet well but tended to shear better, instead of the low non-volatiles liquid originally recommended. This indicates the necessity to maintain flexibility in the application of the well-tried dispersion techniques.

Other high speed mixers

Apart from the use of scraper blades, the main types are based on the simple types described above with additions, e.g.:

(a) Combined heavy duty and high speed mixers. These usually have a heavy duty blade system (often a Trifoil arrangement) operating at the lower portion of a mixer containing the product while a high speed mixing blade, arranged to operate about half-way up, is inserted at an angle to avoid any fouling of the shafts. There is no doubt that such a mixer can prove very efficient for various products where consistency presents a problem in the operations.

(b) Rotor stator mixers. These mixers are best used as in-line types. When used in systems where "simple" types have been operating there seems to be no advantage. It is claimed that as the product is being pulled in or pushed out through the slots or slits a shearing (or bashing or smashing) effect results in excellent dispersion. However, in order that the product may be pushed or pulled through the slits a lower viscosity is required than that possible when using a simple high-speed mixer. Therefore the lower viscosity reduces the efficiency of dispersion and nullifies the advantage claimed.

(c) Rotating tank mixer. This is an excellent variation which is very suitable for producing premixes especially for high consistency. The tank rotates on a central plinth and a fixed scraper blade is designed such that material from the side is scraped off and flung into the operating vicinity of the high-speed mixing disc which is eccentrically placed. However, the safety regulations require specific constraints on construction which make this machine quite expensive.

Continuous mills

The continuous mills used in the paint industry are fundamentally of two types:

(a) Roll Mills—the shearing action occurs between pairs of rollers or between one roller and a flat bar.

(b) Sand/Bead Mills—the shearing action occurs as a result of the agitation of small milling media (sand, glass or other synthetic types).

Although there are specialised mills of each type which can cope with very coarsely prepared mixes and act as comminuting mills these are the exception rather than the rule. For most mills of the continuous variety in the paint industry, a thoroughly prepared premix as previously described is necessary for the above mills to function satisfactorily. Here again it is stressed that the result obtained will be very greatly dependent on the efficient (or otherwise) manner in which the premix has been prepared.

The main difference between the two types of mills is in the consistency of the premix for the best results. The roll mill performs most satisfactorily with a premix of very high consistency—indeed this is as high as is possible to prepare provided the other requirements (e.g. stability) are incorporated, with due precaution. Sand/bead mill premixes are of a lower consistency because of the mill construction but nevertheless should be as high as the particular model will allow.

Continuous mills have usually been fed with premixes that mainly have been prepared batchwise so that adequate control of the quality of the premixes is possible. However the continuous preparation of premixes would not be impossible with a number of in-line premixer blades especially with the more easily dispersed materials.

On the other hand, as the discharge from these mills is stable, completion could be continuous. At present however batchwise working is the normal procedure except for some isolated instances.

Roll mills

The triple roll mill is the most widely used multi-roll mill and the principles of operation can be readily appreciated from Fig. 9. Other multi-roll mills (e.g. five and seven roll) can be understood by extending the arguments for the triple roll mill.

The three rolls, feed, middle and apron, rotate in the directions indicated but at different speeds, e.g. if the rolls were 12 in. diameter and 30 in. long the speed of the feed roll may well be 30-40 r.p.m. The middle roll in some of the older models could be rotating at 1.5 times that of the feed roll and the apron roll at 1.5 times that of the middle roll. However the rate of production increases with higher roll speed ratios and the newer models tend to have a ratio of 2 and even 3.

The feed is through a "hopper" formed by the feed and middle rolls with two end plates specially designed to ride on the rolls and prevent spillage out of the sides. The gaps between the rolls are maintained under hydraulic

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pressure at about 1-2 mils.

In operation, the very high viscosity of the stabilised pigment mill base combined with the different roll speeds ensures differential laminar flow of the paint entering the feed middle roll nip. The close proximity of the rolls determines a very highly efficient shear stress action on the thin ribbon of material passing through. All the material eventually passes through both nips (where the action is similar) although a portion tends to be returned to the feed by residual pick-up of the rolls. A well designed and properly placed take-off apron can usually be nearly 100% efficient.

The triple roll mill is probably the most efficient dispersing machine available to the paint industry but certain precautions have to be observed.

Good training and supervision is necessary for the operation of these machines to avoid unnecessary damage to the rolls, which will wear even with the best care. If the rolls wear unevenly a number of problems arise which can be very troublesome unless the cause is known. To avoid any doubt it is advisable to check the milling efficiency at a number of points along the length of the roll. If the results are not exactly the same then it is obvious that some parts of the rolls have worn to a greater extent than others and the expensive process of regrinding the roll(s) will have to be considered.

Premixing for the triple roll mill operations must take into account the necessity for the final high viscosity of the stabilised mix. Although it has been possible to prepare high consistency products on the high-speed mixer, really high viscosity premixes would require not only heavy construction but high horsepower to cope with the forces necessary to move heavily bodied materials. The most suitable premixer for triple roll mills would be a heavy duty mixer of the high shear stress low shear rate type. The combination of the latter type of mixer and the triple roll mill would provide a dispersion facility of the highest order—from the quality point of view—because each machine can be arranged to produce absolute laminar flow at highest viscosity.

If a compromise has to be sought for premixing however with a simple type of high speed mixer, then the efficiency should be increased when possible by using a small tank to disc diameter ratio with adequate power. An alternative type that has proved to be quite efficient is the rotating tank with the scraper blade and eccentrically placed high speed mixing disc. Of course power available must also be adequate.

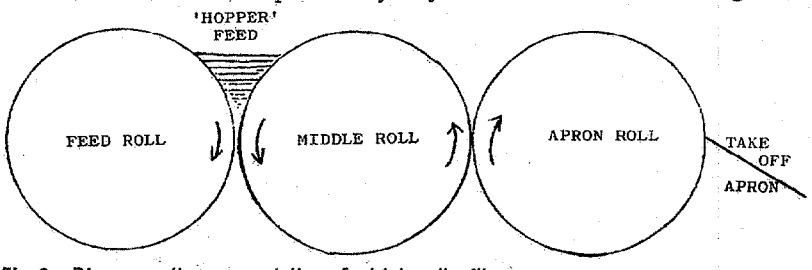

Fig. 9. Diagrammatic representation of a triple roll mill.

Single roll mill

The principles of operating the single roll mill (or bar mill) is diagrammatically given in Fig. 10. The stabilised premix in the hopper feed is dragged through the gap between the roll and the bar and is collected by the take-off apron. The bar which has two or more vanes—depending on the size of the mill—is held against the rotating roll by hydraulic pressure and thus serves a similar role as a roll on the triple roll mill. Actually, however, because the bar is static it is usually necessary (based on the feed composition) for the premix to be a little less viscous than that for the triple roll mill. Nevertheless it is an excellent mill with results almost up to triple roll mill standard and the principles for premixing will be virtually the same as given for triple roll mill manufacture. One major feature however must be noted. The construction allows some paste through at the ends of the bar without being fully subject to the shearing action. This means that some poorly milled material may be collected. However the take-off apron is so designed that the product collected is that quantity apart from the amount at each end that is likely to be poor. The end portions are collected separately and returned to the hopper for further milling.

As with the triple roll mill, the single roll mill requires a well-trained operator and both the bars and rolls must be checked to make sure they are satisfactory. Regrinding the bar as well as the roll may be necessary at times.

For many of these reasons and because both mills are rather labour intensive, the triple and single roll mills are somewhat out of favour with paint manufacturers who are now most likely to be "sold" on the sand mills.

Sand mills

General

Sand mills usually denoted as continuous sand or bead mills are basically cylinders in which small milling media

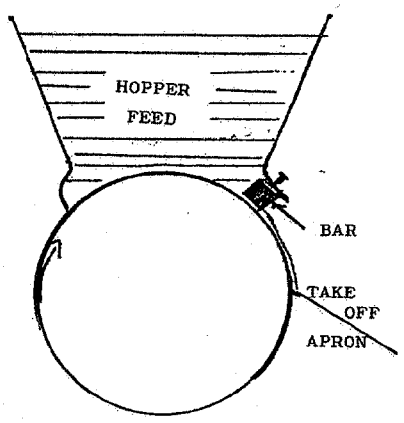

Fig. 10. Diagrammatic representation of a single roll mill.

such as sand, beads, etc., are actuated by means of disc type impellers while a premixed pigment (or other particulate solid) base in a resin, or similar, solution is passed through for processing. The base is discharged in a milled or dispersed state depending on the formulation and procedure.

A number of different suppliers extolling their own design have made the choice of mill an interesting if difficult one. Whatever claims are made however some basic points apply, not only to the different suppliers models but also to modern developments. Caution however is necessary in assessing the changes in performance a modified design may cause. For all models though it can be said that improved dispersion results from:

(a) A higher consistency of premix—provided that the machine is designed to cope with the high consistency;
(b) Smaller milling media—although lower limit is usually 0.8 mm;
(c) Greater quantity of milling media (i.e. increase in ratio of milling media to pigment base);
(d) Faster agitation of the milling media—this necessitates adequate horsepower and will affect temperature and pressure;
(e) Slower passage through the mill—also affecting temperature and pressure.

Other factors which may affect output rate and quality especially with the later models are:

(i) Design of screen;
(ii) Design of the impellers;
(iii) Composition and size of milling media. These of course are common to all three types denoted later and therefore may be discussed before the mills and processing methods.

Milling media

The general principles previously noted for milling media hold but special considerations may apply as under:

Shape: The media are subject to high speeds when the mill is in operation

therefore they must be, or approximate to spheres.
Size: For different purposes different sizes may be used in the range (of diameters) 0.6-3.0 mm.
Composition:

(a) Natural. The only natural milling media for sand mills is Ottawa sand, with a particle size of about 0.8 mm ± 0.2 mm and almost spherical. Its relative density is of the order of 2.6 and is generally sufficiently hard for pigment dispersion. New deliveries of this material should be recirculated in a resin solution through the mill and a screen until extraneous dust and jagged edges have been removed.

(b) Synthetic. Synthetic types include glass and ceramic types.

Glass has proved to be an excellent milling medium and can be obtained in various sizes. Precautions with respect to relative density are necessary because some suppliers just send stocks obtained from various places and are unaware whether lead is present in the composition. Wear is not so greatly different no matter what type of glass is used unless poorly shaped specimens are used in the first place.

Steatite would be satisfactory if a suitable supply is obtained.

Alumina would be suitable only if fused, not sintered.

Zirconia was recommended at one time. This oxide of zirconium was considered to be ideal because its relative density was around 5.6. However, the type available had been prepared by a sintering process which caused it to wear much more rapidly than would be suitable and the processed material finished up with an unwanted extender. Moreover, the same media within a month of use had caused considerable wear on the sand mill in which it was being investigated. Had the zirconia been prepared by a fusion process wear might not have been so pronounced both of the mill and media, while the high relative density could well have proved an advantage in spite of the large and variable sizes of the media.

Zirconium silicate prepared by a fusion process in the form of small beads has proved the most suitable medium yet. Whether it is a pure zirconium silicate or a physical fusion of the oxides of zirconium and silicon is not established and probably does not matter. However, with a relative density of 3.8 it has shown quite a number of advantages over glass with respect to milling efficiency:
(a) The higher relative density produces results faster for the same quality or a better quality for the same time of milling;
(b) There is less wear on the mill and the media wears far less than glass to the extent that although the medium may be dearer than glass originally, the reduced wear makes it effectively cheaper.

There is one drawback however which must be checked. Some poor batches of these zirconium silicate beads have shown a variable hollowness. In many batches the degree of hollowness has been slight but where this has been excessive not only does this affect the relative density but many beads may actually break up. Therefore, although these beads are recommended, they must be checked for the hollowness described.

Sand mill types

There are three main types of continuous Sand Mills: (1) Vertical "Open", (2) Vertical "Closed", (3) Horizontal.

There are other minor variations which include two or more mills in series but the method of operation for the best technical results follow logically from a study of the usual types.

There are quite a number of different models of the above types although most suppliers at present tend to concentrate on the horizontal types.

The differences in construction are mainly concerned with:

(a) Discs—there are a wide variety of shapes of the disc impellers in all three types. Many of the different shapes are claimed to be "scientifically" designed although the writer considers the main idea was to show they are different from others!

(b) Seals—the seals are very important for the vertical closed and the horizontal types and performance should be critically considered.

(c) Screens—the means of separation of the milled paint from the sand was a reasonably simple screen for the original vertical open mill. When the processed materials were shown to be continually building up on the outside of the screen the vertical closed mill was introduced to overcome this. This latter mill operated under pressure and the milled paste was thus pushed through the screen. At this stage a slit or dynamic separator was introduced by Drais and formed one of the methods used in horizontal mills, which however use a variety of different screens depending on the makers' ideas.

Premixing for the sand mill

As the sand mill is a continuous mill it has not been found easy to design one in which stabilisation can occur during the processing of a base passing through the mill. One such mill was designed several years previously but most mills have remained such that they must be fed with a premix that has been stabilised.

Most premixes for sand mills are prepared on high speed mixers and this is satisfactory provided that the principles previously described have been followed. On the other hand it must be stated that the ideal type of premix from a technical point of view would be prepared in a heavy duty mixer especially when organic pigments are being processed. Nevertheless whichever method is used the premix prepared with the proper attention to detail is stabilised to the consistency most suitable to the type of sand mill available. Ideally then the stabilised premix will be processed (milled or refined) through the sand mill in one pass. If more than one pass is necessary then unless the pigments are particularly difficult to mill or there is some other known factor, the procedure adopted should be reviewed including the formulation of the initial premixing, the stabilisation procedure and the Sand Mill charge (of milling media).

Sand mill—milling media charge

The Vertical Open Mills are the only ones which are recommended to be charged with sand. The quantity advised is best initially left to the supplier's ideas but can readily be adjusted by the dispersion technician. Usually the sand level is just above the upper plate but below the lower part of the screen. This loading allows a large space over the sand into which it can be allowed to rise when the mill is operating and a stabilised base is being pumped into the bottom of the mill for processing. This means of course, as for many other mills, that the pigment base will tend to occupy a space much greater than the voids of the milling media when at rest. The extent of space is dependent on the rate the premix is being introduced into the mill. The faster the pumping rate the higher the sand rises and the greater the ratio of pigment base to sand. The faster rate also means less friction with the sand in the mill because the greater amount of base means more lubrication with the sand. Therefore within the mill the temperature tends to drop with high throughput although the sand grating on the screen produces a certain amount of heat by friction. This however may be disregarded except for very heat sensitive materials. However, the main result of faster throughput is a reduced efficiency of milling. Therefore the rate must be adjusted primarily for milling efficiency and compromise only effected when absolutely necessary for any of the other parameters.

The vertical closed mills are in the main an extension of the open types but fully enclosed to enable the whole to operate under pressure. The screen enclosure still permits the milling media to move but this is more restricted in some models which have a slit type of separator acting as a dynamic separator. The main differences between the usual vertical closed and open mills is that sand is not recommended—instead glass or other synthetic types—and the closed mills operate under pressure to enable bases of high consistency to be processed. Here again the initial charge may be left to the supplier but only as long as the

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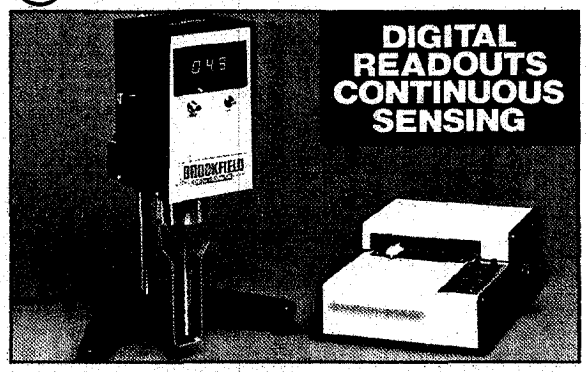

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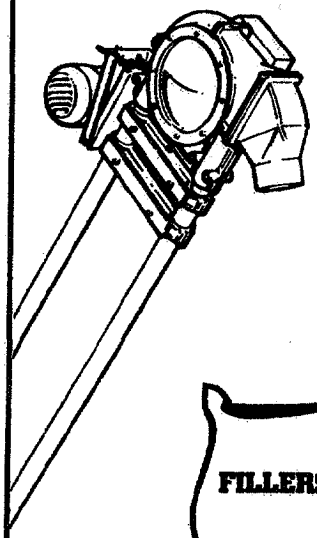

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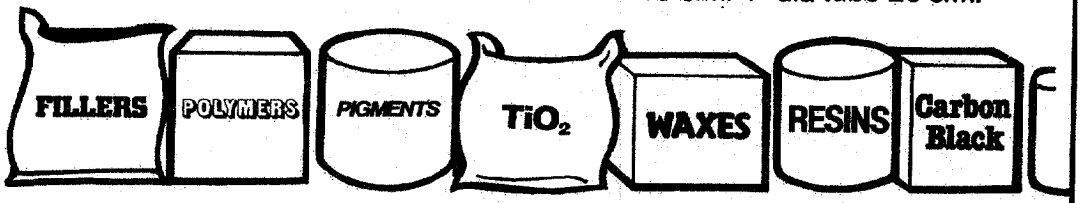

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initial trials are made because there are certain factors that should be initially established.

The usual recommendation for milling media for vertical closed sand mills of the larger type has been an equal mixture of 2 mm and 3 mm glass beads. It must be remembered that in these mills there is a large column of beads and consequently an extremely heavy weight at the lower end of the mill. This heavy weight must be rotated by the impellers for the mill to operate. The smaller the beads the greater the packing together and therefore the more effort required initially to start the mill and one reason for the mixture of sizes noted above is that 3 mm beads were placed at the lower end. This allowed a less compacted condition than would be possible with 2 mm beads, and therefore an easier and freer start. However, the major point with freer starting is that all beads—especially glass—should always be left with ample lubrication preferably with a resin solution that can be used in the next batch. It is dangerous to leave only a minute amount of lubrication because the heat evolved can volatilise the solvent and burn the resin leaving a charred mass of resin and glass!

The horizontal mills have the great advantage that the weight of beads are not involved in the start of operations. The beads are in a horizontal cylinder, through the centre of which is the shaft actuating a number of disc or other types of impellers rotating in a vertical plane. Therefore gravity does not have to be overcome to anything like the extent when starting vertical mills.

The main characteristic distinguishing the horizontal sand (or bead) mill from the vertical models is the high milling media to premix ratio that may be designed. Some suppliers have indicated a range of suitable milling media apparent volumes to be between 70% and 90% of the total empty mill volume, the remainder of the space being occupied by the pigment paste passing through the mill. However, as the main advantage of the horizontal mill is the high ratio of milling media to pigment paste (the higher this ratio the better the milling action) the writer considers that a mill charge of apparent volume equivalent to less than 75% of the mill volume would be unrealistic except for very special circumstances. Moreover a charge of more than 85% must be treated with caution because of possible problems with respect to pressure and temperature.

Comparison of the three sand mill types

All types of continuous mill will of necessity require a premix and, as has been previously stressed, the better the premix the better the result (or the easier it is to obtain the final result). All models similarly will of necessity require a stabilised premix, which in operation will pass through the mill and be subjected to a milling action by the media.

The simplest sand mill, i.e. the vertical open, usually performs quite adequately. The degree of milling may be controlled by reducing the rate of processing to improve the quality while increasing the rate where the premix is so good that milling occurs quite easily. It would be quite difficult however to cope with materials of high consistency or thixotropy.

The vertical closed mill can deal with higher viscosities and therefore basically must be regarded as a better mill.

The horizontal mill however, with the possible very high milling media to mill paste potential, has the means of producing the best milling from any mill of the sand mill group. However, a number of these mills supplied by various manufacturers show differences in the design of discs (impellers), seals and screens and these will determine to a large extent some of the potential. If the screen is such that the area is fairly limited the pressure may build up quickly if fast pumping is tried to increase the rate of production. Similarly the temperature may tend to rise. Thus the enormous benefits derived from the use of the horizontal mill must be tempered with a greater degree of control.

Scale-up

An interesting feature in the comparison of vertical mills and horizontal mills is the scaling-up effect. To a large extent the vertical mills can be regarded as scaling up directly, i.e. a mill producing a given production rate will, if scaled up n times, give near enough n times that rate, provided that the materials are of a reasonable viscosity. With the horizontal mill there is a specific factor to consider and that is the pressure in the chamber as well as the temperature of the material as processed. The latter is determined (and therefore restricted) by the formulators and technicians. The former—the chamber pressure—must not exceed that maximum clearly defined by the manufacturers (usually 1.5 Bar). Therefore provided there is no doubt that both the pressure and temperature are fairly low, when processing given materials, scaling up on a larger machine will allow production to be scaled-up in the same ratio. If however one is at or near the limits scaling-up will be governed by those limits, viz. if a model is to be increased in size n times the production rate (as a result of pressure and/or temperature limits) will be increased by a factor $n^{2/3}$.

However, when considering the high-class automotive gloss enamels for which these mills are ideal it has been shown that the horizontal mills tend to perform 2-3 times better than vertical mills of the same shell size, provided the rheology is not abnormal.

It is understood that Draiswerke have models which are interchangeably vertical and horizontal mills because of their special design. These specific types must be regarded as being more like the horizontal mills described above than the vertical ones.

Co-milling and mixing methods

It was stated at the start of these notes that problems could well occur if pigments of different particle sizes and properties were milled together. So far the dispersion notes have been applicable as a general guide. It would be fitting at this stage to look at the milling of more than one pigment.

Consider the preparation of a light blue paint. This could be accomplished by two methods:

A. (i) a phthalo blue pigment is milled satisfactorily (i.e. according to the given dispersion techniques) in a particular resin or other vehicle.

(ii) a white pigment is similarly milled in the same vehicle.

(iii) the products from (i) and (ii) are mixed to give a certain defined formulation.

B. The blue and white pigment mixed in the ratio given in the formulation are co-milled in the vehicle to give the final formulation arrived at in A(iii).

For the benefit of this exercise it is necessary that the principles advocated should have been observed to ensure the milling has been up to the standard required. In spite of this however it will be seen that the two paints prepared as above are different. Indeed B will invariably result in a deeper shade. The difference will be marked such that if it were necessary to tint the pale shade to the depth of the other it could be that an extra 20% of the blue pigment (and sometimes even more) would be necessary as an addition (in the form of a dispersion).

Another feature of interest is that if the two samples A & B prepared as above were carefully checked on ageing it would be seen that sample *A* will deteriorate more rapidly than the other.

The reason why sample *B* is deeper and more stable than sample *A* has been the subject of much curious speculation. However in the opinion of the writer a consideration of the stability of colloids, colloidal suspensions and suspensions is the simplest and most direct approach.

Although it is often stated that "colloidal solution" as a term refers to a dispersion in which the particles have a maximum size or a given size range, it is really correct to consider that as particles in a suspension show a decrease in size, the case becomes that of a suspension becoming a colloidal suspension. This in turn becomes a colloid or colloidal solution. This means that a dispersion with two or more different particle sizes will exhibit a state in which some particles are more colloidally dis-

persed than others. Moreover, by virtue of their being smaller particle types the more colloidal dispersed materials are also more intimately associated with the continuous phase. This is because, for equal quantities, the smaller particle size materials have larger total surface areas than the larger particle size types.

When any colloidal suspension is treated with a foreign material an instability occurs which is usually manifest in a degree of flocculation depending on the suspension and the added material. The more intimately connected with the continuous phase, the greater the effect of instability. Therefore when two different particle sized materials are present (in the experiment *A* above), even in the same continuous phase, the mixture results in a flocculation of both types, but the more colloidally dispersed, i.e. the blue pigment having the smaller particle size, will flocculate to the greater extent and therefore the colour value will be less, i.e. paler.

If however the larger particle size pigment (the white in this experiment) were milled with an even larger sized pigment (say a given large particle sized oxide or chrome) and also used to prepare a similar formulation by mixing, the latter would be the deeper colour. This is because in this case the white pigment was the more colloidally dispersed. Moreover again the mixing method will produce a material that is less stable than the co-milling method because once a flocculation has started it usually accelerates, unless a protective colloid is present. This will be noted at a later stage.

It is important to consider the advisability of co-milling as against mixing methods from both the colour and stability viewpoints. Usually the small particle sized pigments are the more expensive and therefore economics would demand some consideration.

Fig. 10 shows the development of colour in both procedures (co-milling and mixing methods) as observed in a typical experiment using a small particle sized blue organic pigment which was somewhat difficult to mill and a larger particle sized white (titanium dioxide) pigment rather easily milled.

In the early stages the white pigment was much more readily dispersed and effectively exhibited smaller particle sized performance than the blue pigment which remained as larger aggregates until stage "M". At this point both the white and blue pigments behave as though their aggregates or clusters are of the same size and therefore flocculating to the same degree. Beyond "M" the blue pigment is progressively dispersed to a smaller particle size (or cluster) than the white pigment and the typical disparity between co-milling and mixing methods is exhibited.

The position of "M" depends on a number of factors including the particle sizes of both materials, their ease of dispersion, the degree of dispersion and the concentration of each particulate solid in their respective continuous phases.

If two dissimilar pigments having similar particulate distribution and ease of dispersion were co-milled and mixed as in the previous experiments an interesting point could arise. Both pigments being equally associated with the continuous phase would flocculate to the same extent giving the same colour effect by mixing as by co-milling. However flocculation will ensure that the total colour will have been reduced with the result that the mixing method preparation will have less opacity than the co-milled material and as mentioned previously will deteriorate more rapidly.

The flocculation characteristic with mixing methods is an important feature in dispersion procedures and must not be disregarded. In the process of stabilisation, discussed previously, the highly pigmented base will readily flocculate even on addition of a material equivalent in composition to the continuous phase unless and until substantially reduced in pigmentation. Even so reduction in the mill is a wise precaution as recommended.

Another important procedure in which carelessness may cause virtually irremediable flocculation is the tinting procedure. Both the tinted material and the tinter should be at the lowest pigment concentration composition possible and stirring should be vigorous to avoid major problems.

Flocculation occuring as a result of the prolonged duration of an interface due to inefficient mixing has been mentioned. Therefore additive incorporation must be precise.

Protective colloids are certain compounds which tend to retard the flocculation process because of an adsorption and spatial effect. These materials are mainly cellulose types such as nitrocellulose, ethyl cellulose and cellulose acetate butyrate. Other similar materials are available and in various grades. Choosing the best material may therefore involve many trials but will prove a worthwhile exercise especially when dispersing a pigment in a poorly wetting material. In such cases the additive is included in the milling base.

Where the protective colloids are part of the formulation, e.g. in nitrocellulose paints they do enable mixing methods to be used, because, although there is an initial flocculation, further degradation is retarded.

It should be noted that pigments which are readily degraded in long milling processes, can still be co-milled with pigments which require lengthy dispersion procedures, by adding when the longer dispersion process is completed. In this way the final shorter milling process is a co-milling which is always the more satisfactory process for general properties.

When a large number of pigments have to be co-milled it may be advisable to mill them in a given order. Start with the most difficult and when satisfactory add the next difficult and so on. This procedure will generally provide a better dispersion (and is often much faster) than if an attempt were made to mill all at once. However this would not necessarily apply to products which do not require the most stringent dispersion.

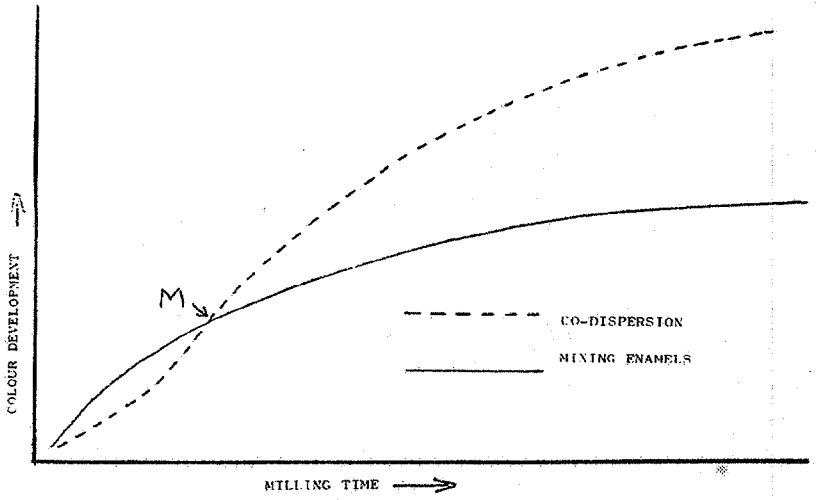

Fig. 10. Development of colour with co-milling compared with mixing.

Additives

Some materials are called "Additives" although in actual fact they should not so be called because they are a fundamental part of the formulation, without which the final product would fail to function or could not be used. Examples are driers. With respect to defoamers, coalescents, flow agents, etc., one tends to be in a "grey area" where possibly

the choice of the original materials may not have been sufficiently discriminatory to avoid the necessity for modifying additives. Of course the occasional emergency which requires additive treatment must be recognised.

There has, however, been an increasing tendency to use additives at the drop of a hat without checking on the cause of the problem. It must be emphasised that additives are generally specific—the more specific, the more effective and vice versa. Again it must be recognised that specificity may also result in unexpected side reactions in spite of great care in selection. Allied with this is the property of some additives to exhibit their properties only in a given stage in the process and to reverse—seemingly—its properties if the process is allowed to continue. This is exemplified in the following example (referring to fig. 12):

AA represents the maximum colour development or degree of dispersion possible theoretically from a specific particulate solid or pigment.

BB represents the *practical* maximum dispersion possible with the machines available.

Ideally then an additive acting as a wetting agent would then allow production to proceed as shown in curve SA rather than SB which is the practical production line with the given plant. However to date no such wetting agent additive has been found. Misleading results though have often been indicated by wetting agents similar to that shown in Fig. 12. Early trials results tend to show the milling to follow the curve SIC so that the full practical results could be achieved in a shorter time than usually possible, which of course would be worthwhile. Unhappily it is more usual for the milling with the wetting agent to follow the path SIED. At point E there is no advantage in using a wetting agent additive while beyond that point the additive behaves as a flocculant with the result that is less well developed in colour and less well dispersed than without the additive!

It has been grudgingly accepted that the use of excess of a wetting agent may result in its being effective mainly as a flocculant. This however is not the full story and it is stressed here that every wetting aid is potentially a flocculating agent with the latter effect being its main function and wetting being only incidental. The major example of this is Soya lecithin used as a flocculating agent to cause soft settlement (rather than a hard compact settlement) from decorative paints. Somewhere along the line the properties of soya lecithin were deduced to include wetting but real evidence on this score is lacking. Soya lecithin has for the most part been used in long oil alkyds type paints. As the alkyds are excellent for wetting properties, the real reason for the inclusion of soya lecithin must be ascertained. Where the material has been included in industrial types serious flocculation problems have arisen.

There are of course certain additives which are claimed to be absolutely necessary. In such circumstances it is very necessary to ensure that the right type and grade is used, otherwise it will be seen that further additives must be used to counter the unwanted side effects of the original additives and so on. Eventually a formulation can be arrived at which is mainly additive in character! This is not so far fetched when it is considered that many will tend to seek additives to overcome defects which are not investigated thoroughly. Examples are those resulting from poor mill base formulation, poor stabilisation techniques and the like. When all investigations show that an additive is required it usually is more effective when added at the milling stage.

It must be conceded that some of the more recently introduced materials are very difficult to incorporate because they have been specifically prepared for certain properties without taking into account the necessity for compatibility in dispersion processes which consequently suffer. Recourse is then made to additives! The best approach would be to combine the properties sought in additives into the main raw materials used. Until some such time it will be necessary for dispersion processes to follow the tried techniques (which are quite logical for all to follow) outlined in this series of articles.

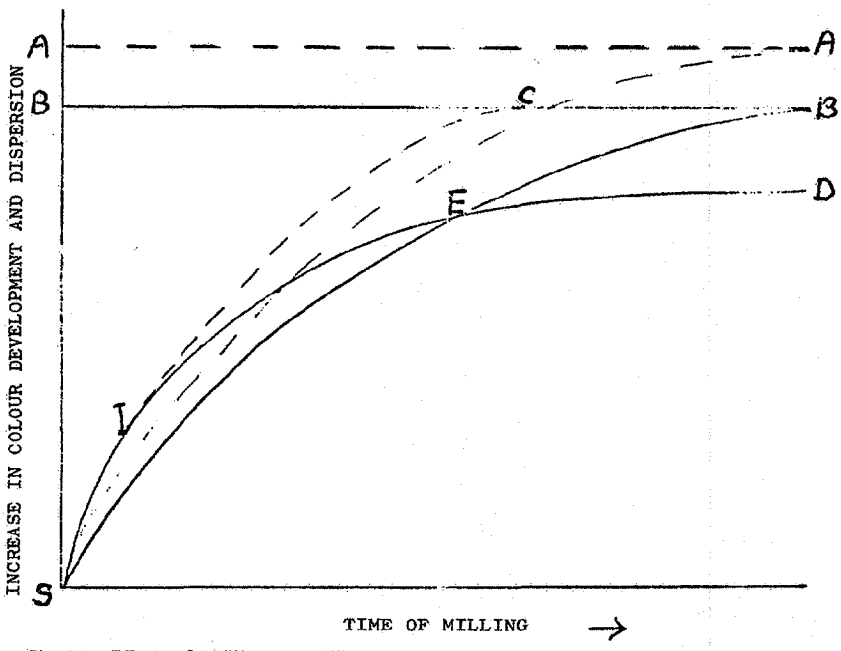

Fig. 12. Effects of additives on milling.

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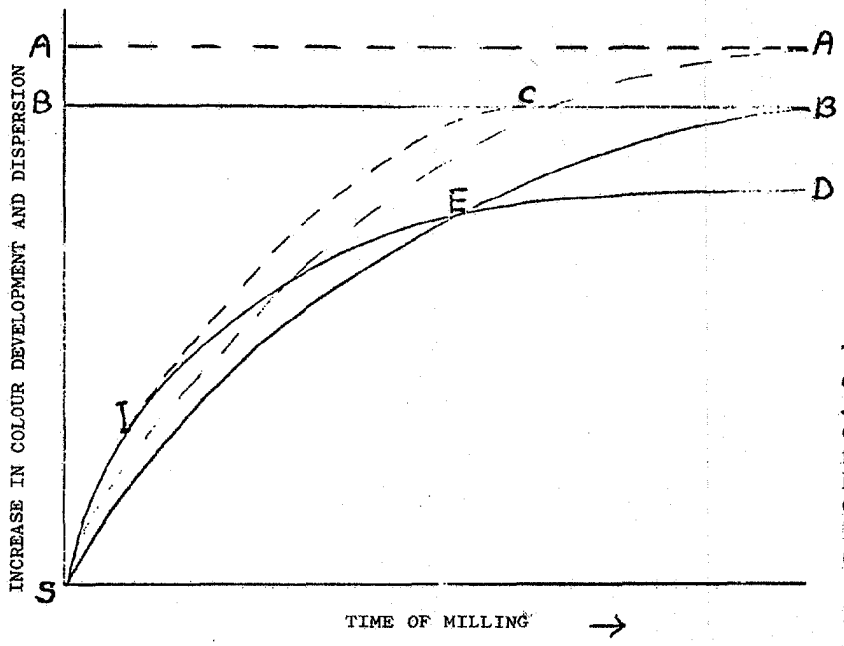

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