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The Role of the Surface in the Behaviour of Titanium Dioxide Pigments*

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A review is presented on the relevance of surface properties in pigment behaviour. It is shown that the majority of titanium dioxide pigments in use have a coating of some other oxide, whose principal role is the formation of an energy barrier for the transfer of excited species from the bulk phase to the organic coating of the paint film. Results of recent studies of dispersion properties and durability of paints against photo-degradation are discussed.

INTRODUCTION

Titanium dioxide pigments are widely used in coating systems where high levels of opacity and hiding power are required, as well as in a wide variety of applications to give whiteness and brightness e. g. in plastics, fibres, ceramics etc. The pigment crystals are nearly spherical and their diameter is about 0.2 μm, corresponding to a surface area of ~ 10 m²/g. In most cases the size distribution of the single crystals is quite narrow, but it is unlikely that when dispersed e. g. in a paint, all the pigment is present as single crystals. Much agglomeration is apparent in virtually all practical applications, and the »particles« are made up of groups of pigment crystals which may have arisen from inadequate dispersion during preparation or flocculation of the pigment after preparation — it is not easy to differentiate between them.

As a powder the pigment occupies about 25⁰/₀ of the available space (75⁰/₀ air) i. e. the pigment volume concentration (PVC) is 25⁰/₀. In an average paint system the pigment has a PVC of 20—25⁰/₀, hence in making a paint we simply replace air by liquid, although the distribution of the solid particles is different in the two situations.

A study of pigment dispersion therefore involves an understanding of the formation and properties of the solid-liquid interface. In the early stages of the process the solid/air interface is replaced by one between solid and liquid. The pigment powder consists of aggregates/agglomerates of small particles and mechanical work is performed in dispersing particles into a liquid. The forces that exist at the interface determine the ease with which the process can be brought about. Once dispersed the particles are free to move in their

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new environment, and flocculation is prevented by various chemical and physical processes, all of which relate to the character of the solid/liquid interface. It is not surprising therefore that studies of this interface form an integral part of our understanding of the dispersion process, and of those aspects of pigment performance that are dependent on the state of dispersion.

THE PIGMENT SURFACE

The surface of the majority of titanium dioxide pigments is not titanium dioxide. Due to the fact that titanium dioxide is a strong absorber of ultra violet light and acts as a catalyst in the photodegradation of pigmented paint films by sunlight, the surface of most pigments is covered with a layer of one or more inorganic oxides. This layer forms a barrier to the transfer of excited species, formed during irradiation, from the crystal to the organic component of the paint film. The choice of oxide(s) is important since not only must the surface layer be efficient in reducing the catalytic effect, but it must also provide a surface which is compatible with the polymeric components of the liquid medium to ensure efficient dispersion.

An understanding of the chemistry of the coating process is vital to the efficient manufacture and application of titanium dioxide pigments. The chemistry is complex. Essentially the titanium dioxide crystals are brought into contact with a solution containing a hydrolysable salt. The chemical behaviour of both phases is pH dependent, and precipitation of the hydrolysis product on to the crystal surface is controlled by variations in pH, temperature and concentration. Coatings are usually of the order of 10 nm in thickness, are not always uniform in thickness, and may not always completely cover the available surface. Silica and/or alumina are most frequently used, and because the isoelectric points of the three oxides are so different, microelectrophoresis provides a useful technique for studying the coating process. This was reviewed in a paper by the author given at the III conference in this series[1], and in a later paper the mechanism of the precipitation of silica and/or alumina onto titanium dioxide surfaces was discussed[2]. More detailed studies on the formation of silica layers have recently been reported[3] — silica was precipitated from sodium silicate solutions using a method designed to give a dense layer on the surface[4]. Electrophoresis measurements demonstrated the adsorption of the silica species which at low concentrations are in the monomeric form, whereas at high surface concentration ($\sim 5^0/o$) polymerisation occurs at the surface producing a coherent layer.

Studies of the chemical and physical nature of coated titanium dioxide surfaces were reviewed by Day[5]. Provided the surface layer is uniform over the surface and $\sim 5^0/o$ by weight, the chemistry of the outlying surface resembles that of the pure version of the oxide forming the layer, as demonstrated by electrophoretic data[1-3]. This is important since it is this surface at which adsorption of polymers occurs in pigmented paint systems, and therefore determines the configuration of the polymer at the interface, as we shall see later. But in addition to the inorganic coating it is quite common to treat pigments during the final stages of manufacture with an organic compound, frequently a polyol or an amine. This further modifies the chemistry of the surface, and is particularly relevant to the initial stages of dispersion — presumably some or all of the organic is dissolved off the surface during the

later (milling) stages of paint manufacture. An attempt has been made to investigate the effect of organic surface additions on the adsorption properties of the oxide surface, by measuring adsorption isotherms for nitrogen, n-pentane ethanol and water vapour on samples of pure rutile titanium dioxide, silica and alumina pre-treated with ethanol, hexan-1-ol and hexan-1 : 6-diol[6]. The differences between the three oxides in terms of retention and strength of the alcohol adsorption reflect the polarizability of the surfaces, decreasing in the order rutile $>$ alumina $>$ silica. Parallel effects are found with coated pigments provided the oxide layer is thick and uniform[7]. Application of modern spectroscopic techniques (ESCA, SIMS and ISS) to pigment surfaces has yet to be fully developed, but initial results are promising.

RELEVANCE OF COATING TO PIGMENT PERFORMANCE

We shall consider two aspects of pigment performance, and analyse the role played by the surface. The first concerns the dispersion of the pigment into the liquid medium — as mentioned above, the efficiency of this process determines the optical performance of the paint; good dispersion i. e. efficient breakdown of agglomerates, leads to good opacity. Furthermore, good dispersion reduces the photodegradation of the resins in the paint film by absorbing more of the ultra-violet radiation per unit volume of film than when the pigment is flocculated. This is in addition to the catalytic effect of the pigment on this process which is reduced to as low a level as possible by an efficient coating. The durability of pigments is the second effect to be considered below.

Dispersion

The term »dispersion« describes the complete act of incorporating a powder into a liquid medium such that in the final state the pigment particles are uniformly distributed throughout the medium. We identify various stages in this overall process — incorporation, wetting, disagglomeration, and flocculation. During milling each of these processes occurs simultaneously in some part of the millbase, and the final result depends on a variety of factors such as shear rate, millbase surface tension and viscosity, cohesiveness of the powder, and contact angle between liquid and solid, as well as the various interactions that occur between the solid surface and the molecules in the liquid phase. The performance of the final product in terms of opacity and durability, strongly depends on the efficiency of the dispersion process, and therefore on the optimisation of the pigment-medium interactions.

The cohesiveness of the powder is an important parameter in the initial submergence process. Uncoated titanium dioxide pigments are very cohesive — they have a high tensile strength. The surface coating greatly reduces this effect, and aids the breakdown of pigment/air agglomerates when the pigment and medium are brought into contact[8]. Surface moisture also has a profound effect — water bridges between particles increase agglomerate strength.

Once the pigment has been dispersed in the medium it is essential to prevent flocculation so that maximum dispersion is maintained. The stability of colloidal dispersions against flocculation is governed by the forces between the particles. In dilute dispersions it is sufficient to consider only the interaction between pairs of particles, but in the very concentrated dispersions that one meets in coating systems it is necessary to take multiparticle interactions

into account. Most of the published theoretical work has been concerned with pair interaction; little has been written on multiparticle interactions. The DLVO theory of stability provides an adequate understanding of the behaviour of dilute systems provided the repulsive forces are purely electrostatic in origin. Essentially the electrostatic repulsion is a result of the charge on the particle surface. For titanium dioxide in aqueous media this is relatively simple to define — the charge arises from the acid-base character of the surface hydroxyl groups which are neutral (no surface charge) at pH ~ 5.5[9]. At pH < 5.5 the surface is positively charged, and negative at pH values above the zero point of charge. If the surface is coated with alumina it will have a zero point at pH = 8—9, and with silica at pH = 2—3, with many other variations possible for mixed oxide coatings. These phenomena also influence the adsorption of surface active species from solution, hence the ultimate particle charge. A similar situation arises in principle for non-aqueous liquids of moderate to high dielectric constant, in which there is still a significant degree of ionization.

But in hydrocarbon media the extent and nature of the ionization is less readily defined. For ionic materials that are soluble in hydrocarbons there is a small but significant degree of ionization, but the ionic concentrations are ~ 10^{-10} — 10^{-12} g ions/litre, and this implies a very diffuse electric double layer. For this reason it is more obvious that multiparticle interactions have to be considered since even at fairly low particle concentrations there is overlap of electric double layers throughout the system. Another consequence of the low ionic concentration is the very small number of charges associated with each particle, and a marked dependence on adsorbed moisture, particularly for oxides, has been reported[10]. There is no simple relationship between particle charge/zeta potential and amount of surfactant adsorbed, for these hydrocarbon systems. The limited data have been reviewed[11]. Very often one observes a maximum in the plot of zeta potential versus surfactant concentration, the potential decreasing over a range for which the amount of surfactant adsorbed remains constant. It is difficult to explain these effects, although for certain systems an attempt has been made. Fowkes proposed that the relative acidity of the particle and the liquid phase determines the sign of the particle charge; there is a transfer of protons across the interface, which is strongly influenced by the acid/base nature of the surface and of the additives in the liquid phase[12]. Titanium dioxide particles dispersed in solutions of alkyd resin in xylene exhibit a positive charge, whereas in melamine resin solution they are negative[13]. The change in sign on changing the chemical nature of the surface has also been demonstrated with coated titanium dioxide pigments in alkyd resin solutions[14].

The most useful attempt to describe the stability of concentrated systems has been made by Levine[15,16], who concluded that electric double layer effects are unable to provide the necessary energy barrier for dispersions in hydrocarbon media. A similar conclusion was reached from experimental observations of the stability/opacity of dispersions of titanium dioxide pigments in alkyd resin solutions[14]. Hence, one must search for another source of repulsion. In solvent paint systems it appears that the adsorption of the resin at the pigment surface plays a dominant role in the resistance to flocculation. In present day technology a variety of high molecular weight compounds (alkyd resins, block and graft copolymers) are used in organic coating systems, and the role of the

adsorbed polymer is called »steric stabilisation«. In this context we are par-
ticularly interested in the thickness of the adsorbed layer, the configuration of
the polymer chain, the fraction of segments adsorbed and the segment density
distribution, both normal and parallel to the surface. This is illustrated in the
work of Joppien and Hamann[17] who studied polymer adsorption from aqueous
and hydrocarbon media on to pigment and filler surfaces, and related the
structure of the adsorbed layer to dispersion stability in paints.

Efforts to relate flocculation to resin adsorption in terms of the quantity
adsorbed and molecular configuration at the surface, have been relatively
successful[18]. An interpretation of the optical performance of alkyd paints
pigmented with titanium dioxide was made by Franklin et al.[14]. Having
established from electrophoresis and opacity measurements that the surface
charge was not the controlling factor in flocculation, a study was made of the
adsorption characteristics of the resin using pigments coated with different
levels of silica/alumina such that the surfaces created varied from predo-
minantly silica (acidic) to mostly alumina (basic). Interpretation of the adsorption
isotherms indicated that for the silica surface the resin molecules took up a
parallel orientation close to the surface, thus making little contribution to
preventing flocculation. On the other hand for the alumina coated surface the
resin only made contact with its limited number of acid groups, the remainder
of the molecules being extended into the liquid medium and providing a steric
barrier to flocculation. Thus it was established that resin configuration at the
surface plays a role in promoting stability to flocculation in the paint.

Durability

The need for good dispersion to minimise the photo-degradation of paint
films pigmented with titanium dioxide has already been stressed. To relate
the degree of dispersion or the extent of flocculation/aggregation in the paint
film to its stability to decomposition during exposure to sunlight has been the
objective of recent work in our laboratories.

Several techniques are available that give an indication of the degree of
flocculation in a paint, e. g. sedimentation, chromatography, lamp filament
colour, etc., but basically these are qualitative tests which are useful for
formulation purposes. A more accurate assessment may be made by using the
technique of infra-red backscatter which we have developed. The measurements
are made on a dry paint film. Flocculates will, as a result of their large size,
preferentially scatter long wavelength radiation, and the amount of scattered
light depends on the size and number of the flocculates, i. e. on the degree of
flocculation of the paint. The contribution to the long wavelength scattering
by well dispersed particles is small, hence the measured backscatter is due to
the relatively small number of large particles, whether aggregates, agglo-
merates or flocculates. A plot of backscatter against film thickness is linear
for thin films and the slope is termed the »flocculation gradient«. Measurements
on a series of paints covering a range of flocculation levels were reported by
Balfour and Hird[19] and a model based on an uneven distribution of particles
in the film was used to interpret opacity data for air-drying alkyd and stoved
alkyd/melamine systems.

Another property of a dry paint film which reflects the state of pigment
dispersion is its gloss. The level of gloss depends on the refractive index of the

film, the texture of its surface, and the angle at which the surface is illuminated. Defects in the surface of a paint film that are of the order of 0.1 μm in height are responsible for a decrease in gloss and since this dimension is similar to that of a TiO_2 pigment particle it can be seen that the pigment plays an important role in influencing the gloss of paint films. The relation between gloss and flocculation has been demonstrated, and also for gloss retention of films exposed to ultra violet light[20]; the higher the flocculation gradient the larger the decrease in gloss on exposure.

The destruction of a paint film by exposure to sunlight can be quite a lengthy process, and as pigments improve development work becomes intolerably slow if only natural weathering data are available. Several machines are used to speed up the process, but the relationship between natural and accelerated weathering is often not easily defined. The product developer needs a rapid method for assessing the durability of his pigments, which will reflect their behaviour in the natural environment. An attempt has been made to put the catalytic effect of a pigment on a quantitative basis, and quite successfully in this respect is the photo-catalysed oxidation of propan-2-ol to acetone. Experiments with nine commercial titanium dioxide pigments show an activity sequence which is closely similar to that obtained from conventional accelerated weathering tests on paint film[21]. This reaction might well form the basis of a rapid method of assessing the photoactivity of pigments, and an investigation of the mechanism of the catalysis reaction has been reported[22].

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SAŽETAK

Uloga površine u ponašanju pigmenata titanijeva dioksida

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Revijskim pregledom novije literature pokazana su saznanja o utjecaju površine na ponašanje pigmenata. Na primjeru pigmenta titanijeva dioksida pokazano je da ih se većina u primjeni u industriji boja presvlači slojem nekoga drugog oksida. Svrha je toga površinskog sloja oksida da bude prepreka prijenosu pobuđenih vrsta, nastalih fotoaktivacijom u zrnu titanijeva dioksida, na granicu faza organskog filma. Teorijska diskusija znanstvenih saznanja odnosi se na svojstva disperzija i na otpornost konačnih proizvoda prema fotodegradaciji.

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