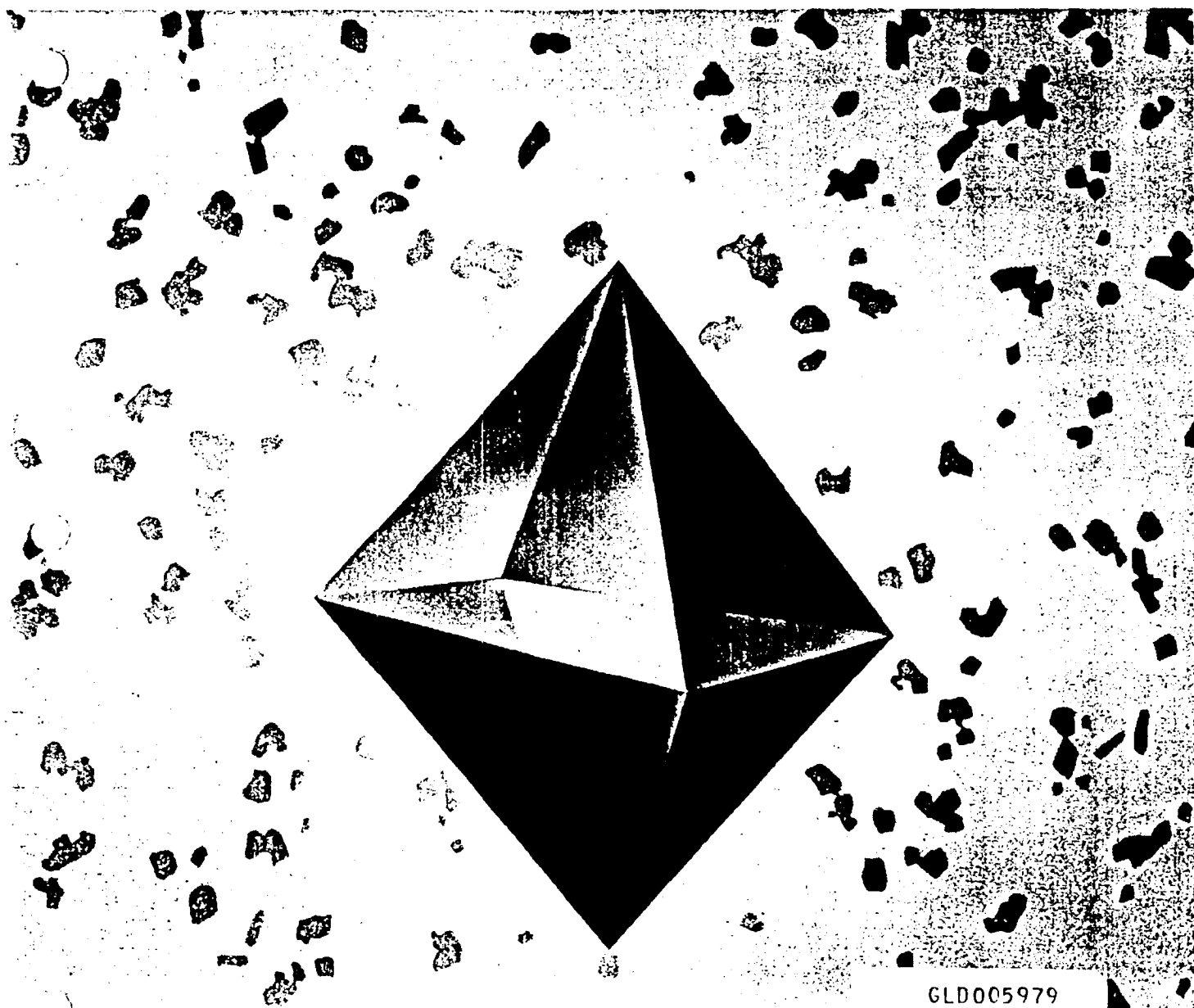


ISHIHARA TIPAUQUE NEWS

TIPAUQUE PIGMENTS FOR CHAMPION OF PERFORMANCE & WHITENESS



GLD005979

T-701

**THE RELATIONSHIP BETWEEN PARTICLE SIZE AND
OPTICAL PROPERTIES OF TITANIUM DIOXIDE**

While common rock sugar is colorless and transparent, a mass of the smaller crystals appears white. On the other hand, tobacco smoke from a mouth appears whitish, while smoke direct from the cigarette is bluish. In the same way, in a white pigment such as titanium dioxide, the optical properties vary according to the particle size. The important factors in white pigments are the scattering and absorption of light. The absorption of light depends on an inherent property of the pigment material and is affected by the kind and amount of impurities contained. In the scattering of light, there is a complication in that it varies according to the refractive index, the size of particle and the concentration of pigment in paint. With regard to the scattering of light, there are first discussed a few formulae concerning optimum particle size which show which particle size scatters light most efficiently. The second section is a discussion of the treatment of optical properties of a paint film by P. Kubelka and F. Munk. Lastly some theories of Mitton, Bruehlman and others are considered.

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1. The effect of particle size on the scattering of light

1) Scattering formula for unit particles

It is well known that light consists of electromagnetic waves. The following three cases may be considered with regard to the relationship between the particle size (d) of pigment particle and the wave-length (λ) of light, i.e.

$$\begin{aligned} d &> \lambda \\ d &\sim \lambda \\ d &< \lambda \end{aligned}$$

- (i) $d > \lambda$: Particle size larger than the wave-length of light.

This is called the geometrical-optical region. In this region, the large surface of the particle has greater scattering power because scattering of light is caused by reflection from the surface of particle.

If the scattering power is S ,

$$S \propto \frac{1}{d}$$

- (ii) $d < \lambda$: Particle size smaller than the wave-length of light.

This is called the region of Rayleigh's scattering. When a white light of unit intensity is radiated to a spherical particle of size d , Rayleigh's formula becomes as below, showing the radius vector of light scattered:

$$I\theta = \frac{9\pi V^2}{2R\lambda^4} \left(\frac{m^2-1}{m^2+1} \right)^2 (1 + \cos \theta)$$

where θ : angle between the direction of incident light and the direction of observation of the scattered light,

$I\theta$: intensity of scattered light in the direction of θ ,

V : volume of the particle,

R : distance between the particle and the observation point,

m : refractive index of the particle.

Integrating the above formula over all θ , the total scattered light, S becomes:

$$S = 24\pi^2 \left(\frac{m^2-1}{m^2+1} \right)^2 \frac{V^2}{\lambda^4}$$

$$\therefore S \propto d^6 / \lambda^4$$

It is seen that in the Rayleigh's region in which the particle size is smaller than the wave-length, S decreases sharply in proportion to the sixth power of d . In this region, since the intensity of scattered light is inversely proportional to the fourth power of wave-length of light when the particle size is constant, the scattering of light of short wave-length increases at a greater rate than light of long wave-length, therefore the particles appear bluish. This is the reason why the smoke from a cigarette is blue: a white pigment may also show a bluish shade if it has a small enough particle size.

rette is blue: a white pigment may also show a bluish shade if it has a small enough particle size.

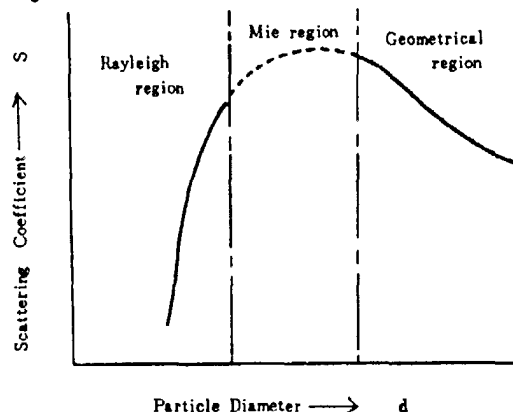
- (iii) $d \sim \lambda$: Particle size similar to the wave-length of light.

This is called Mie's region and the following formula is obtained:

$$S = \frac{d^2 \pi}{4} K (\alpha m)$$

The above is illustrated in Fig.1.

Fig. 1



It is seen that the scattering of light has a maximum value where d is $\lambda/2$, and the optimum particle size is also fixed at $\lambda/2$.

2) Optimum particle size

There is much literature on the subject of optimum particle size, both theoretical and experimental.

- (i) Jaenicke's formula:

$$d_{opt} = \frac{0.9\lambda}{nB\pi} \left(\frac{m^2+2}{m^2-1} \right)$$

$$m = nP / nB$$

nP : refractive index of pigment

nB : refractive index of binder

- (ii) Weber's formula:

$$d_{opt} = \frac{\lambda}{2.1(nP - nB)} \text{ approximately}$$

- (iii) Mitton's formula:

$$d_{opt} = \frac{\lambda}{1.414 nB\pi} \left(\frac{m^2+2}{m^2-1} \right)$$

- (iv) Clewell's formula:

$$d_{opt} = 0.61\lambda / nB \text{ approximately}$$

Using these formulae, the optimum particle size in microns at $\lambda = 550m\mu$ may be calculated as follows:

Refractive index: $TiO_2(R) = 2.74$, $TiO_2(A) = 2.56$,

$ZnS = 2.37$, $ZnO = 2.02$, linseed oil = 1.48,

water = 1.33, air = 1.

Jaenicke's formula is derived from Mie's theory and relates simply to the scattering of light by unit particles, and Mitton's formula is an empirical formula which also takes into account the pigment volume concentration.

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Jaenicke's equation			
	in linseed oil	in water	in air
TiO ₂ (R)	0.23 μ	0.23	0.23
TiO ₂ (A)	0.27	0.25	0.24
ZnS	0.30	0.27	0.26
ZnO	0.47	0.39	0.31

Mittton's equation			
	in linseed oil	in water	in air
TiO ₂ (R)	0.18	0.18	0.18
TiO ₂ (A)	0.21	0.20	0.19
ZnS	0.24	0.22	0.20
ZnO	0.37	0.31	0.25

Weber's equation			
	in linseed oil	in water	in air
TiO ₂ (R)	0.21	0.19	0.15
TiO ₂ (A)	0.24	0.21	0.17
ZnS	0.30	0.26	0.19
ZnO	0.49	0.38	0.26

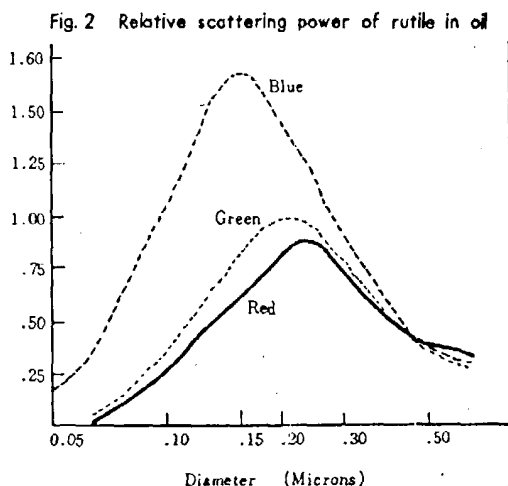
2. Optical behavior of paint film

As a pigment is usually used with a vehicle, it is necessary to study the behavior of light in a film containing vehicle and pigment. In paint films consideration must be given to problems such as pigment volume concentration (PVC), the relative refractive index of vehicle pigment or a mixed system of white and colored pigment, etc.

1) The tint of paint films

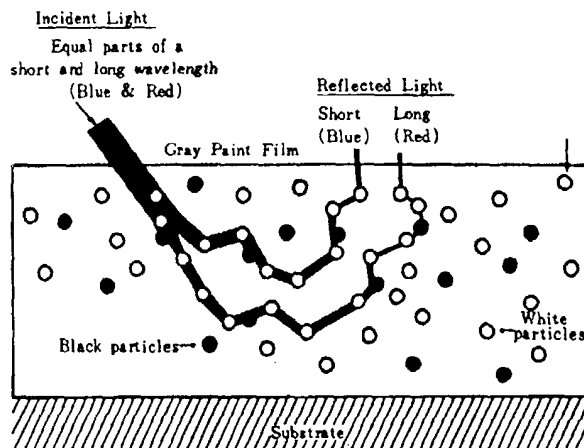
As seen from the equation for optimum particle size above, the light scattering power of a uniform particle size changes in accordance with the wavelength of light. It becomes greater in direct proportion to the refractive index to the medium.

Bruehlman⁶ reports that in TiO₂ (R) [see Fig. 2] the scattering of light in the blue region is greater than that in the red and that scattering power is very sensitive to the particle size.



Thus, when particles are in a paint film the size of the particles is in general measured by observation of the color of paint film. Bruehlman shows that when light enters a paint film containing black and white pigments, it is absorbed by the colored pigment and scattered by the white pigment. The type of reflected light is shown in Fig. 3.

Fig. 3



Owing to the scattering power of TiO₂, the intensity of blue light scattering increases when the particle size becomes smaller. Thus when a mixture of blue and red light is passed through a mixed paint film of TiO₂ and carbon black the reflected light appears bluish due to the longer path length of the red light and its greater absorption by carbon black.⁶ From the increase in bluish hue in a mixed paint film of TiO₂ and carbon black it is concluded that TiO₂ has the smaller particle size. The same theory can be applied to the fact that a higher PVC in a TiO₂-carbon system gives a more bluish hue.

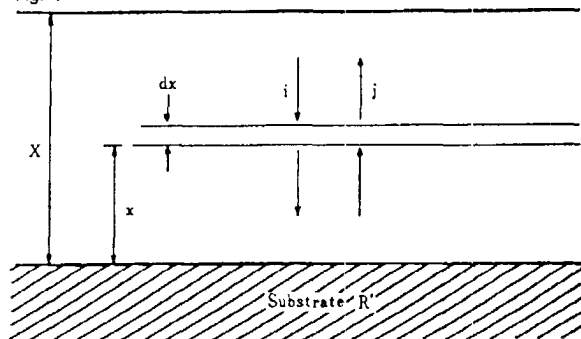
2) Optical equations relating to paint films

Many investigators have presented equations for determining the percentage reflection coefficient, and the ratio of transmittance of light for a film. The following equation is based on the Two Constant Theory of P. Kubelka and F. Munk.⁷

A differential equation is obtained from consideration of a minute thickness dx at a point x from the underside of the film, the scattering coefficient of light which passes through dx (S) and the absorption coefficient (K), and this equation is solved to give an equation which gives a measure of the reflectance of film.

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Fig. 4



Solving the differential equation

$$R = \frac{\frac{1}{R_{\infty}}(R^1 - R_{\infty}) - R_{\infty}(R^1 - \frac{1}{R_{\infty}})e^{SX(\frac{1}{R_{\infty}} - R_{\infty})}}{(R^1 - R_{\infty}) - (R^1 - \frac{1}{R_{\infty}})e^{SX(\frac{1}{R_{\infty}} - R_{\infty})}}$$

Where

R = Reflectance of paint film

R^1 = Reflectance of substrate

R_{∞} = Reflectance of paint film having an infinite thickness

X = Thickness of paint film

From above

$$\frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad \text{or} \quad R_{\infty} = 1 + \frac{K}{S} - \sqrt{\left(\frac{K}{S}\right)^2 + 2\left(\frac{K}{S}\right)}$$

Mitton⁸ gives the relationship, illustrated in Figs. 5-7. As seen from the above, R_{∞} depends on S and K , and R_{∞} decreases when K/S increases.

When a paint film is on a black surface, the reflectance R_B becomes:

$$R_B = \frac{1}{a + b \coth SbX}$$

The equation may be obtained when $R^1 = 0$ in the equation derived from the Kubelka and Munk theory, as shown in Fig. 8.

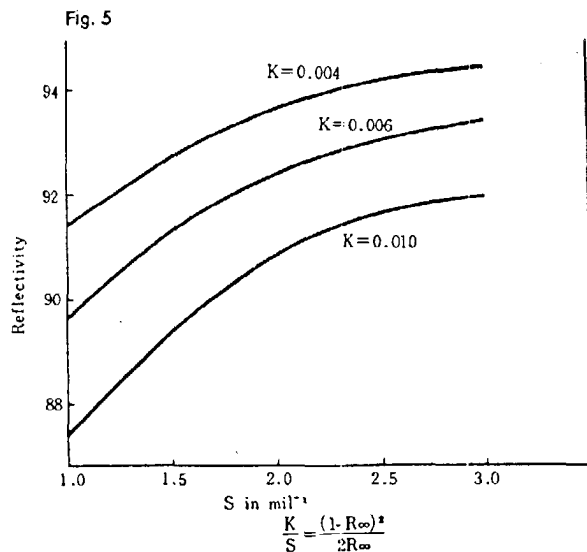


Fig. 6

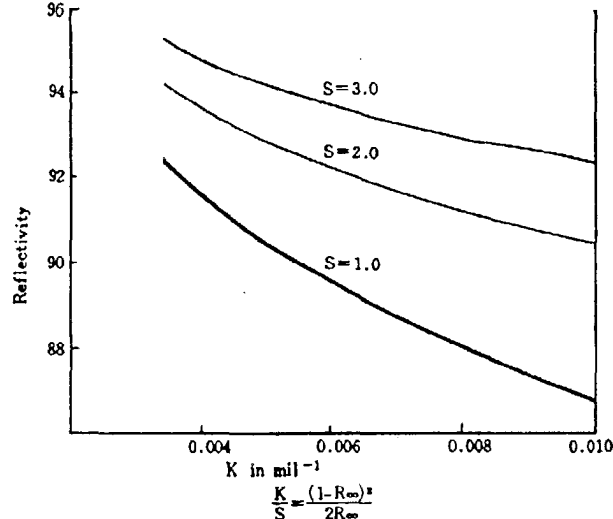


Fig. 7 Reflectivity as a function of S and K

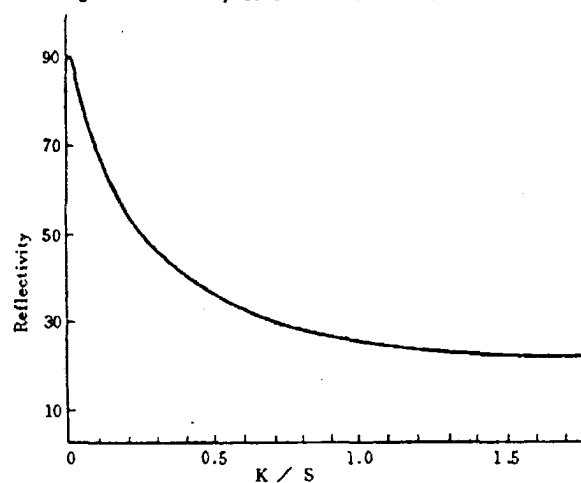
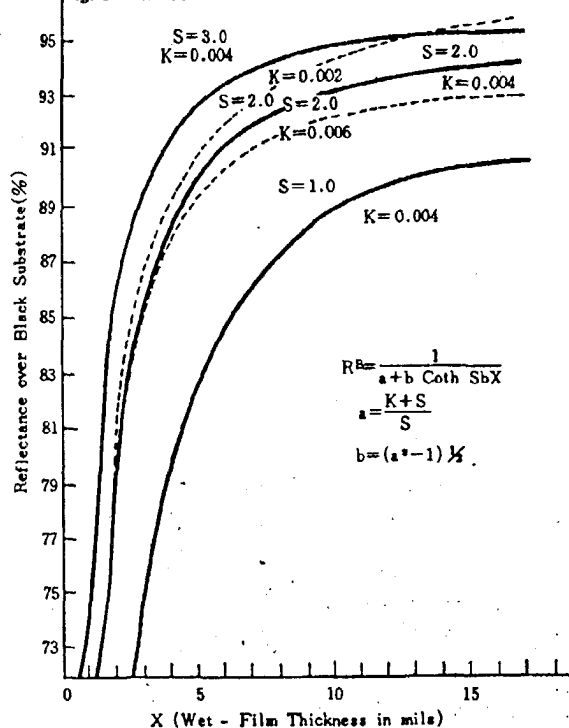


Fig. 8 Reflectance versus film thickness



3. Optical properties of pigment particles

The scattering of light by unit particles, the optical behavior of paint systems and the Kubelka and Munk Theory have been described. Mitton et al. have developed a theory based on the Kubelka and Munk theory concerning the optical properties of hiding power and brightness which often raise many discussions when paint films are used in practice.

1) Relation between the physical properties of pigment particles and S and K

The principle of additivity of S and K can apply in general to paint systems. A paint system consists of white pigments, colored pigments, extenders, vehicles and the like, so that S and K of the whole system are the sum of Si and Ki of respective substance⁹:

$$\frac{C_1K_1 + C_2K_2 + \dots + C_nK_n}{C_1S_1 + C_2S_2 + \dots + C_nS_n} = \frac{K}{S}$$

The scattering coefficient S is a function of the relative index of refraction, particle size, particle size distribution, degree of dispersion and PVC of pigment.

It is considered that the absorption coefficient K depends on chemical impurities and the crystal structure defects of the materials as well as the chemical bond and crystal structure.

A characteristic of TiO₂ pigment is its high absorption coefficient for ultra violet light and its small absorption of light in the visible region. The elimination of impurities and lattice defects in TiO₂ crystals makes the absorption coefficient smaller for all wave-lengths of light.

2) Relation between S and K in the paint film components

A white pigment has a small K value. The S value

of pigments of which the refractive index is low, such as ZnO and PbO, is considerably smaller than that of TiO₂, and that of CaCO₃ and SiO₂ is very small. The S value of a black pigment is very low and consequently the value of K is very high for all wave-lengths.

3) Relationship between tinting strength and K and S

For the measurement of tinting strength of TiO₂, a standard TiO₂ pigment and lamp black are kneaded with castor oil to make a standard paste. The sample TiO₂ pigment to be tested is kneaded in the same way, with lamp black and castor oil. The amount of lamp black used in the sample TiO₂ paste is adjusted so that the brightness of both pastes becomes identical; thus the tinting strength can be determined from the difference in the amount of lamp black used. In this case, "S" of the paste can be said to be dependent on TiO₂ and "K" of the paste on lamp black. Since the same lamp black is used in both the standard and the sample and the same weight of TiO₂ is used in both, the scattering coefficient "S" of TiO₂ will decide the tinting strength. If the TiO₂ particle size is small the paste has a bluish hue as described above.

4) The relationship between "hiding power" and K and S

"Hiding power" may be determined by measuring the contrast ratio of a dry paint having a uniform film thickness. It is a function of S and K^{10,11,12,4} and the opacity becomes greater at a constant value of S as the value of K increases. Mitton gives the relationship between PVC and hiding power for many white pigments and shows that the relationship is similar to that between S and PVC.

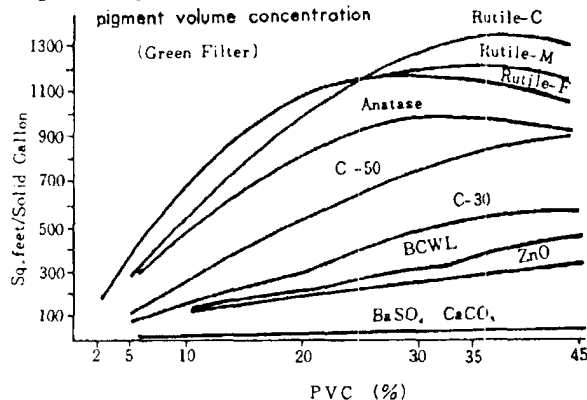
Table 1. Physical properties of materials

Material	Index of Refraction (560mμ)	Average particle size (μ)
(1) Rutile TiO ₂ -fine particle size-Rutile F	2.373	0.225
(2) Rutile TiO ₂ -medium particle size-Rutile M	2.737	0.275
(3) Rutile TiO ₂ -coarse particle size-Rutile C	2.737	0.410
(4) Anatase TiO ₂ -Anatase	2.558	0.238
(5) Titanium calcium (50% TiO ₂) -C-50	2.307	0.611
(6) Basic carbonate white lead-BCWL	2.05	1.02
(7) Zinc oxide-French process-ZnO	2.020	0.505
(8) Titanium calcium (30% TiO ₂) -C-30	2.069	0.495
(9) BaSO ₄ (fine size)	1.641	2.16
(10) CaCO ₃	1.613	1.65
(11) Acrylic resin	1.493	

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The relationships between hiding power and PVC as well as between S and PVC are shown in Figs. 9 and 10.

Fig. 9 Hiding power (sq. ft./solid gallon) versus pigment volume concentration



The refractive index and the average particle size of the pigment used are given in Table 1. The vehicle is acrylic resin in both cases. As shown in Figs. 9 and 10, the curve of S is seen to be similar to that of hiding power, the slight difference in the two sets of curves seems to be due to the difference in K, the higher refractive index materials giving higher values for S. For rutile F, M and C with the same refractive index, the coarser rutile gives the higher value of S at a high PVC and the finer rutile gives the higher value at a low PVC. It is believed that this is caused by the crowding effect.¹² What is the crowding effect? If it is assumed that a pigment consists of only spherical particles having an average particle size, when they are dispersed in a vehicle, they will behave as shown in Fig. 11.

Fig. 10

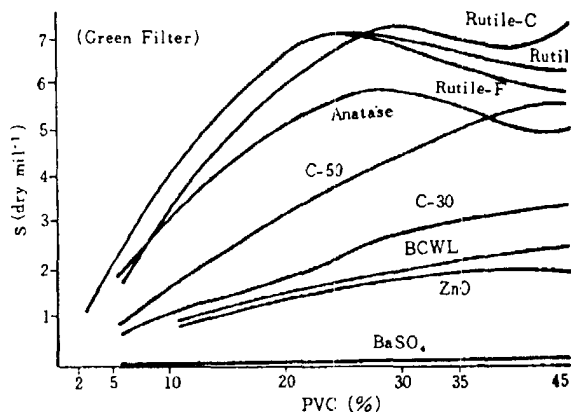
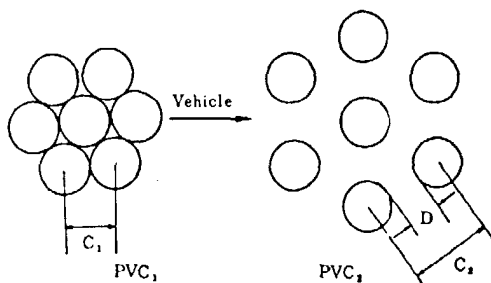


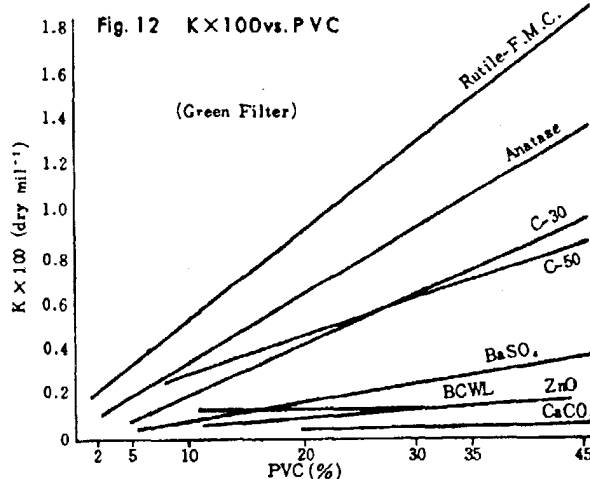
Fig. 11



When the PVC is fixed, the edge-to-edge distance (D) becomes smaller at a smaller particle size and when particle size is fixed, D becomes smaller at a higher PVC. When the PVC value becomes higher and D becomes smaller, two particles can not be resolved optically and will show the same effect as a single particle. Thus a small particle size pigment gives a smaller distance (D) at the higher PVCs and will have a lower scattering coefficient than a large particle size pigment. This will explain the fact that the scattering coefficient curves of rutile F, M and C tend to intersect each other as the value of PVC becomes higher.

The edge-to-edge distance (D) which has a critical value on the S-PVC curve is calculated as approximately 1/2 of the wave-length of incident light.

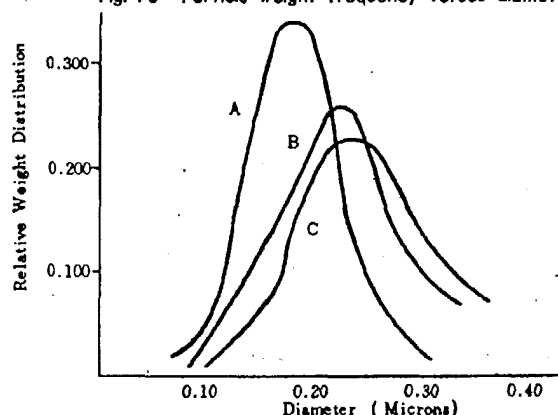
The relation between PVC and absorption coefficient K is shown in Fig. 12.



Bruehlman *et al.*⁵ also report the same result. They determined the scattering power of three rutile TiO₂ samples having different particle sizes and particle size distributions respectively, by varying the value of PVC and the kind of vehicle.

The particle size distribution of a sample of TiO₂ is shown in Fig. 13.

Fig. 13 Particle weight frequency versus diameter



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The results obtained for an appliance enamel and a linseed oil paint are shown in Figs. 14 and 15.

Fig. 14 Scattering power of titanium dioxide in an appliance enamel

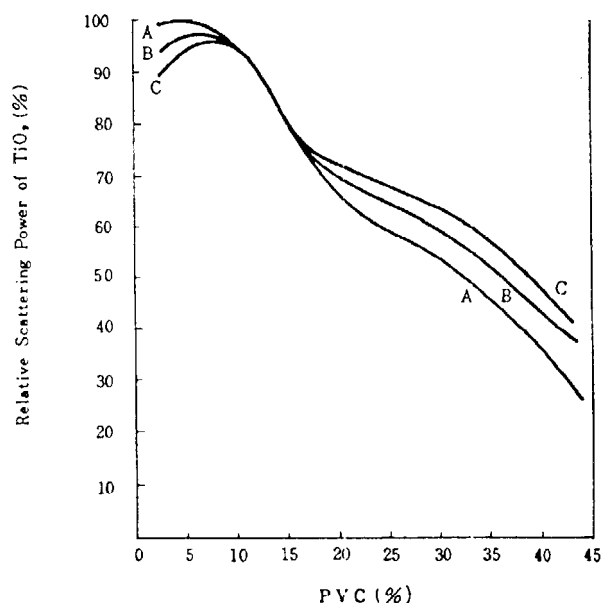
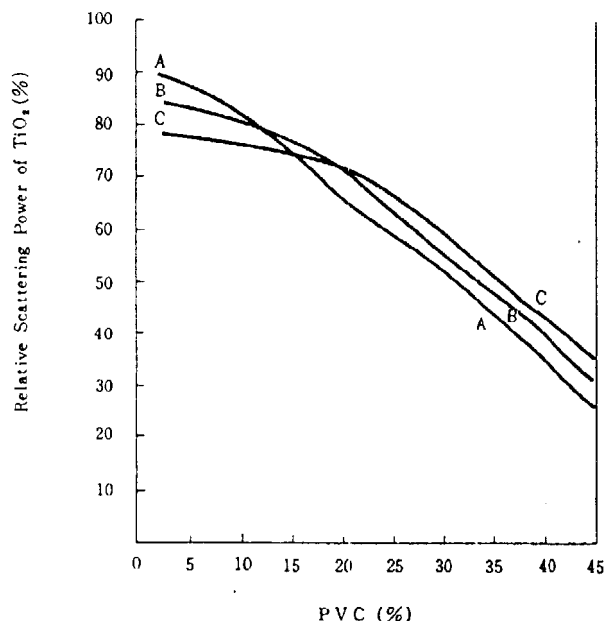


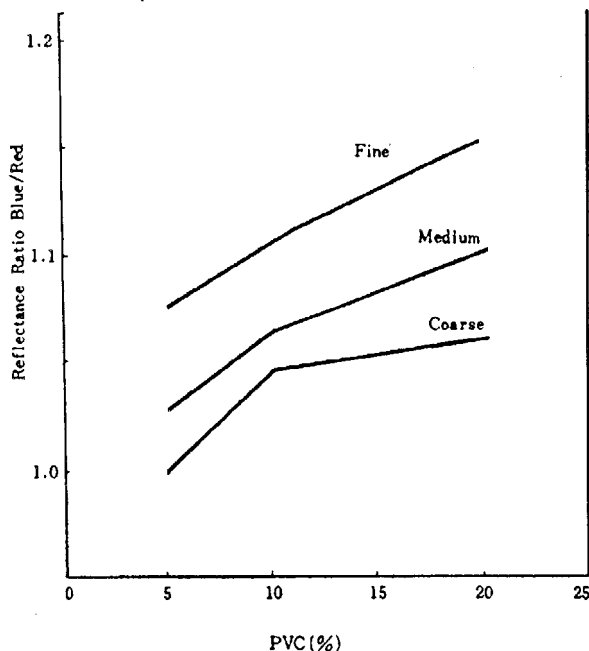
Fig. 15 Scattering power of titanium dioxide in a linseed oil



At low PVC values (below 15 per cent PVC), TiO₂ having the smallest average size has the greatest scattering power; at a medium value of PVC (15-25% PVC), the scattering power of medium size TiO₂ is not so sensitive to the particle size; and at high values of PVC (above 25% PVC), TiO₂ of the largest average size gives the greatest scattering power.

It is found that in a tinted system, the hue of rutile having a smaller particle size looks more bluish and the undertone increases. The hue also becomes more bluish as the value of PVC increases, as shown in Fig. 16.

Fig. 16 Effect of pigment volume concentration and particle size on undertone



Mitton *et al.* give the equation for optimum particle size and the relation between PVC and hiding power or S . They also calculate the scattering coefficient of 10%, 20% and 30% PVC for rutile TiO₂ when the refractive index of the binder $n_0 = 1.50$ and the wave-length of incident light is $540m\mu$ to attain the curve shown in Fig. 17.

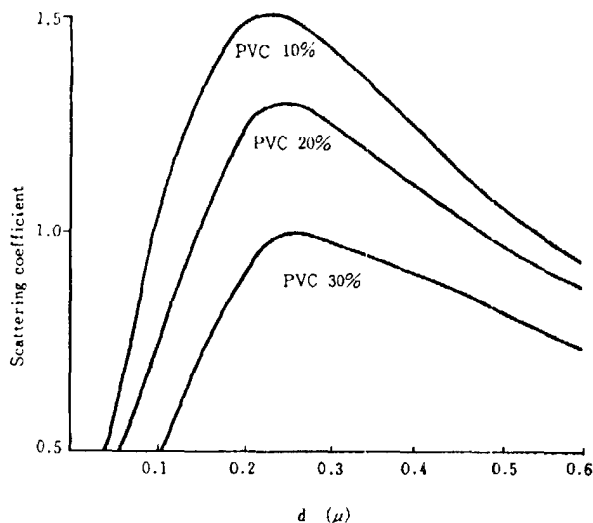
This shows that the scattering coefficient will become lower at a higher value of PVC and that the optimum particle size is approximately around 0.25μ at 30% PVC and about 0.2μ at 10% PVC. The scattering coefficient is only slightly lowered when the particle size is larger than the optimum particle size, but it is reduced sharply when the particle size is smaller than the optimum one. It is preferable then that the average particle size distribution of TiO₂ pigment in practice should be slightly larger than the optimum particle size.

4. Practical application

We have shown that rutile having a larger particle size than optimum is more suitable at higher pigment volume concentrations and rutile having a smaller particle size distribution is more suitable at lower pigment volume concentrations. High PVC paints include emulsion paints, flat paints and modern paints coated thinly with a strong resin. The field of low PVCs include top coat paints, plastics and chemical fibres.

In the past titanium dioxide has had restrictions on its use in paints, but now it can be provided in its most suitable form to meet the requirements of the ink, plastics, rubber, ceramics, paper, chemical fibre industries and various other fields.

Fig. 17 Scattering coefficient versus particle diameter



Up to last year, we have marketed all over the world TIPAQUE R-820 and R-550 having a suitable particle size as rutile for the general use. TIPAQUE R-820 has been and is welcomed for its top-durability and R-550 recommended for the industrial use.

In addition to the two grades, we have developed new rutile-type titanium dioxide TIPAQUE R-780 and R-580 as rutile having a large particle size and R-680 having a small one.

TIPAQUE R-780 is being used mainly for emulsion paints and water soluble resin paints, TIPAQUE R-580 for acrylic paints requiring hiding power and gloss, and TIPAQUE R-680 for plastics and top coat paints.

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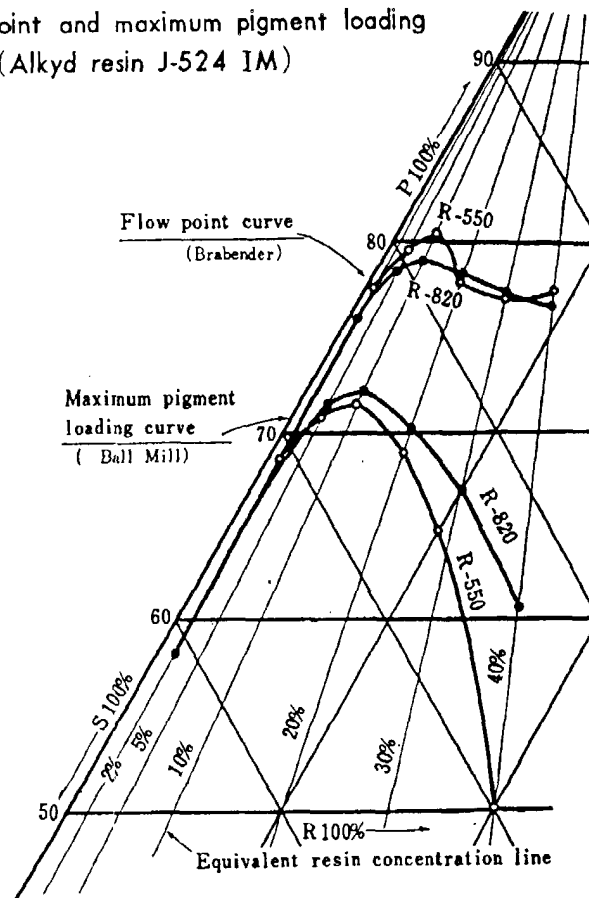
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Notice of Correction:

We should like to correct the errors made in the TIPAQUE NEWS T-602 and T-605 as follows:

T-602: Please replace Fig.2 in page 4 with the following figure.

Fig. 2 Flow point and maximum pigment loading point (Alkyd resin J-524 IM)



T-605: Please rectify the 9-10 lines of explanations for tw in page 4.

Correct one: "...the faster entrance to the voids between pigment particles and..."

Erroneous one: "...the faster entrance of pigment into voids and..."

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