Some Optical Problems of the
Paint, Varnish and Lacquer Industry

By R. J. BLACKINTON

THE art of making paints is one of the oldest, yet by some quirk of fate one of the latest to be given careful scientific study. Probably the reason lies in the complexity of the chemical and physical problems involved, but more likely is it due to the adequacy and simplicity of the two-component mixture of linseed oil and white lead that has served the general protective coating demands so well for the past two hundred and fifty years. This pigment, basic lead carbonate, acted not only as a light reflectant, but also as an oxidation catalyst or "drier," a buffer to absorb acid decomposition products, a film strengthener, and, after reacting with free fatty acids, as a plasticizer and water repellent.

White lead, however, had two serious handicaps: it darkened badly in sulfurous atmospheres, and it was very inefficient as a light reflector; i. e., it was not very opaque. In attempting to improve on these properties a host of problems were uncovered, both physical and chemical. We shall, however, in this article, cover only the optical problems involved in films of transparent varnishes and lacquers and opaque, pigmented films. The phenomena of gloss, degree of whiteness and hiding power will be discussed. The physical laws governing these problems will be presented and an attempt made to interpret them on a practical level.

GLOSS

The values of specular reflection are determined by the well-known relations developed by Fresnel, which

simplify to

$$\frac{I}{I_o} = \left[\frac{n-1}{n+1}\right]^2$$

when the incident light is perpendicular to the surface whose index of refraction in air is n. For other angles of incidence the function is different, but the constants are the same, so that the gloss of a smooth film at a given angle is determined solely by its index of refraction. For example, the average varnish or lacquer film has an index about the same as a light crown glass (1.52), which corresponds to about 4.2 per cent at 90 degrees. The most refractive commercially used resins are the highly chlorinated diphenyls, which run as high as 1.67, giving 6.2 per cent normal gloss. The available range of true specular reflections for smooth films is therefore rather limited, the highest being only some 50 per cent greater than the minimum.

In spite of this apparently narrow range there is a vast difference in the psychological responses to specular gloss. This field is generally divided into at least three groups: objective gloss, which is the true specular reflection discussed above, subjective gloss, and sharpness-of-image reflection. (See *Fig. 1.*)

Objective gloss is best demonstrated by the visual difference in gloss between two films of the same resin.

(A) Full specular reflection
Distinct mirror images
Full gloss

(B) Full specular reflection
Indistinct images
Wavy surface

(C) Semi-gloss
Distinct images
Partially filled with transparent "pigment"

(D) Dull
No images
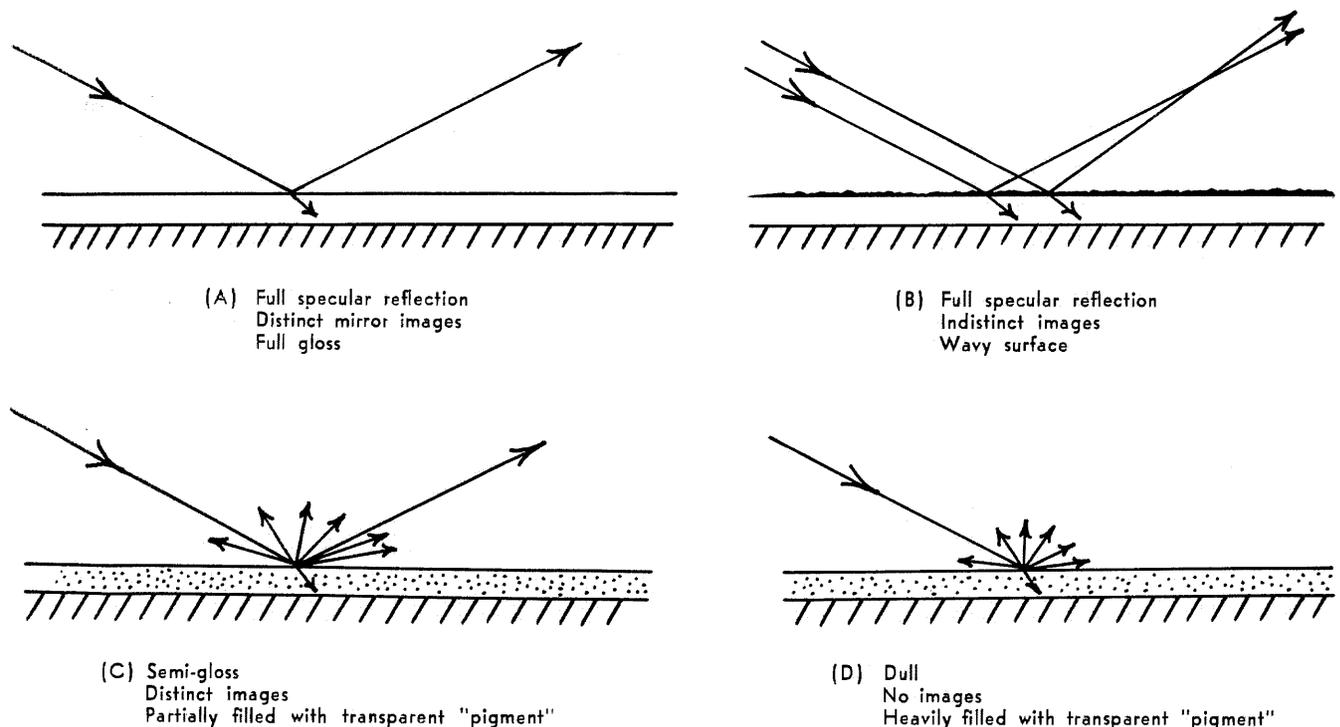Heavily filled with transparent "pigment"
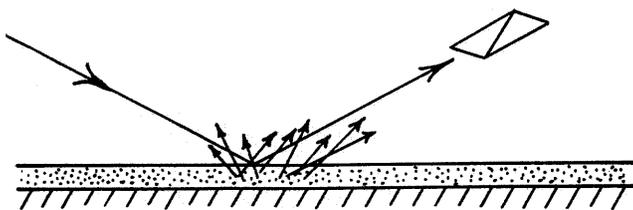
FIG. 1. Specular reflection of clear films.

FIG. 2. Measuring subjective gloss with Nicol prism, using background of pigmented film as reference. Specular reflection of opaque pigmented film. Glossy white enamels have low subjective gloss. Glossy black enamels have high subjective gloss.
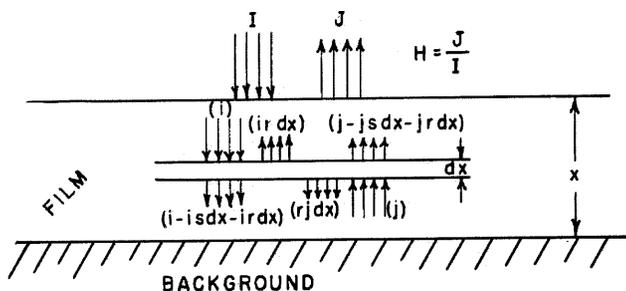

FIG. 3. Derivation of the Kubelka reflectance equation.

one of which is pigmented white and the other black. The latter always appears much "glossier" than the former, although the specular gloss of the two must be equal, and indeed is, by specular reflection measurements. The difference is attributed to the fact that the eye judges gloss by comparing the specularly reflected light with the surrounding field, which is governed by the diffuse reflecting power of the pigment. Various attempts have been made to record this psychological value and some are on apparently sound principles. One rather ingenious direct method is to use a Nicol prism to evaluate the degree of polarity of the light reflected at the average polarizing angle of reflection. This gives reasonably good results, since the specularly reflected light at this angle is largely polarized, while that diffusely reflected is not. (See *Fig. 2.*)

Specular reflection is reported in terms of approximately absolute values, since the meter is calibrated with polished black glass ("carrara glass") of known index of refraction. Using Fresnel's formula, the specular gloss is calculated for the angle under measurement. The usual angle for specular gloss measurements is 60 degrees incidence and 60 degrees reflection. For many camouflage paints a grazing angle of 85 degrees incidence (5 degrees off the plane of the test panel) is used. This is necessary, since too fine grinding of the flatting agent may give a poor distribution of reflected intensities and may give telltale glancing of sunlight.

The flatting agents or materials used to reduce specular gloss of clear coatings must have approximately the same index of refraction as the dry film in which they are used, in order not to impart opacity along with dullness. Many materials have been used, such as cornstarch, the bi- and tri-valent metal soaps such as calcium, zinc, aluminum and barium stearates, oleates or palmitates. Some hard insoluble natural waxes, such as carnauba, have also been used successfully. One of the most successful materials is a recently developed dehydrated silica gel, so carefully dehydrated that it is nearly an

aerogel. This type is desirable, since it is non-settling, chemically inert and close enough in index of refraction to the average lacquer and varnish films to be practically invisible. In use these materials are simply tumbled in a pebble mill with the vehicle until the desired particle size obtains. Extremely fine grinding is undesirable, since the particles must be large enough to give irregularity to the surface of the film; on the other hand they must be kept below the limit of naked-eye resolution in order to give a pleasingly smooth surface.

REFLECTANCE

Considering now the case of diffuse reflectance from pigment particles within the film, investigations have been made into the theoretical aspect of reflectance in terms of film thickness. Many methods of approach have been tried, and one, by Rhodes and Fonda in 1926, arrived at the proper although abridged logarithmic relation by an over-simplified algebraic approach. Kubelka and Munk in 1931[*] seem to have been the first to derive a comprehensive relation on a reasonably sound basis. Their approach can be most easily explained by the accompanying schematic figure, which represents the various light intensities on a differential element of the film. The incident and reflected light rays are separated from each other for simplicity.

As light penetrates the differential element, part is absorbed, part reflected and the remainder transmitted. This happens to the reflected light coming upward exactly as for the incident light traveling downward. In *Fig. 3*, i represents incident intensity, j reflected intensity, s the coefficient of absorption, and r the coefficient of remission. The latter factor is similar to absorption in that it impedes transmission, but instead of being converted to heat the light is merely reflected. It includes the Raleigh light-scattering effects as well as reflection and refraction from particles much larger than wavelength dimensions.

If we subtract the light intensity traveling downward away from the element from that incident downward upon it, we shall have the differential change in incident light intensity:

$$-di = (i - isdx - irdx + rjdx) - i = -(s+r)\,idx + rjdx$$

and likewise

$$dj = (j - jsdx - jrdx + ridx) - j = -(s+r)\,jdx + ridx$$

By definition, absolute reflectance, H, is the ratio of the total reflected light to that incident on the surface:

$$H = \frac{J}{I} \text{ or } dh = d\left(\frac{j}{i}\right).$$

These are simultaneous first order differential equations relating reflectance to film thickness. The solution is

$$H = \frac{H_{\infty} - H' + H_{\infty}\left(1 - H'H_{\infty}\right)e^{rx\left(\frac{1 - H'H_{\infty}}{H_{\infty}}\right)}}{H_{\infty}\left(H_{\infty} - H'\right) + \left(1 - H'H_{\infty}\right)e^{rx\left(\frac{1 - H'H_{\infty}}{H_{\infty}}\right)}}$$

where H_{oo} is the ultimate reflectance of a very thick film of the paint and H' is the reflectance of the background.

Before arriving at the final equation above, it was necessary to solve for the ultimate reflectance. This is done by integrating between limits of "o" and "oo" for film thickness. This relation is very interesting in that the ultimate brightness is found to be a function only

[*]"Ein Beitrag Zur Optik Der Farbanstriche," Z. tech. Physik, 12, 593.

of the ratio of the coefficient of absorption to that of remission:

$$H_\infty = 1 + \frac{S}{R} - \sqrt{\left(1 + \frac{S}{R}\right)^2 - 1}$$

It is apparent that for the ideal white pigment the coefficient of absorption, s, must be zero, which means that it would be perfectly transparent if it were in massive form. Since this is not completely realized even with pure chemicals, the value of r must be large to give a high reflectance. To get an actual value for r it would be necessary to measure the coefficient of absorption on the pigment and on the vehicle separately in massive form and then calculate the composite coefficient from the percentage composition of each in the paint film. The absolute value of r would then be:

$$r = \frac{2 H_\infty S}{(1 - H_\infty)^2}$$

The constant, r, as pointed out above, is the sum of the individual effects of true scattering, reflection and refraction. As a pigment is reduced in particle size, these three factors change markedly and individually. Reflection and refraction increase as particle size is reduced until wave-length dimensions are reached, say about 0.5 micron; then they must diminish rapidly, since these phenomena depend upon mechanics of complete wave fronts which must comprise at least the dimensions of a single wave. As the particles are reduced in size below this region, the Raleigh scattering commences. Experiments have shown that too fine grinding of pigments reduces the whiteness and hiding power, which is in agreement with the above theory, since the value of s must remain constant regardless of particle size. It should be emphasized again that a pigment is white only by virtue of the light acting on the surface of the pigment particle and not inside it, for the particle itself is wholly transparent like glass, if it is a good white pigment.

If $r = o$ we have the condition of absorption without reflection which is typical of dyes in solid solution in varnish film. If the absorption band extends clear across the visual spectrum, a jet black will result. This is a most important factor in making jet black enamels. The average person probably does not realize that the paint chemist has as much difficulty, if not more, in making a really black "black" as is encountered in making "pure" whites. Ordinary lampblack is gray by comparison with a modern jet carbon black.

In the manufacture of jet black carbon pigment it is necessary to burn the gaseous fuel at high heat and deposit the carbon rapidly by impinging the hot flames on cold plates. The fine particles of carbon thus formed must be carefully dispersed in a vehicle which will thoroughly wet the individual particles and remove the absorbed layer of air or gases. Under these conditions the particle sizes are kept down to about 25 milimicrons, which are so small, compared to wave-lengths of light, that the coefficient of remission is reduced considerably, and this, according to theory and practice, gives much less reflection or greater blackness.

Before applying the general reflection equation to the problem of measuring hiding power it would be of interest to mention some of the actual methods in use.

The oldest and still most widely used method of determining the hiding power is to brush the paint evenly over a given-sized checkerboard, or other pattern consisting of black and white areas, until the surface appears uniformly light. The weight of paint required to produce this uniformity is used as the index. But who is to say just when the board appears uniform?

Munsell carried out exhaustive experiments to determine the least difference in brightness which the average eye could detect. The ratio of the least detectable increase in brightness to the total brightness had been assumed to be constant by Bouger a century ago and was set at about 0.015 by himself and later by Fechner, after whom this fraction was named. However, the Fechner fraction—with the normal daylight accommodated eye—was found by Munsell to vary from about 0.8 at the threshold of visibility to about 0.018 at average reading brightness. Its minimum value was found to vary from 0.008 to 0.020 in a group of six individuals. In other words neither the constant in the logarithmic stimulus-response relation nor the logarithmic relation itself (Fechner's law) was valid over the full range of vision. However, over the ordinary working and reading range of light intensities from about 10 to 75 foot candles the Fechner fraction of a given individual was found to be reasonably constant.

Further discrepancies in brush-out tests pointed to the probability of a much smaller average value for the Fechner fraction. Exhaustive tests made by Kraemer and Schupp on various patterns of black and white paint-out boards permitted a statistical method of evaluation in which the particular pattern and its position in a group of the test boards had to be named. This experiment showed that with a pattern consisting only of two halves with a shaded line of demarcation between the black and white halves the classical value of 0.015 was confirmed. But a sharp alternate design was much more easily discerned and an average value of 0.004 was found to hold for it.

The necessity of determining the minimum value of the Fechner fraction can be seen quickly if a plot is made of per cent diffuse reflectance against spreading rate in square feet per gallon. In *Fig. 4* a hiding power value of 83 square feet per gallon would be named by an individual whose Fechner fraction is 0.020, but another observer with an acuity of 0.004 would report only 57 square feet per gallon. Thus, if they were competing on a given specification, the second formulator would penalize himself to the extent of about 50 per cent more pigment cost than the first one.

To overcome this trouble two methods are commonly used. A.S.T.M. prescribes a test board under standardized viewing conditions for comparison only with a standard paint. The result merely designates equality, inferiority or superiority. The other test gives spreading rate required to give a designated contrast ratio. The contrast ratio is the ratio of the paint's reflectance over the black base to that over the white base. To determine this value it is necessary to apply the paint over black and over white backgrounds at known rates or film thicknesses and to determine photometrically the reflectance compared to some standard reference. Pure magnesium oxide smoke-deposits are commonly used as the 100 per cent reflectance reference. The logarithms of these two reflectances are plotted against rate in square feet per gallon and the spreading rate is noted where the two convergent lines are separated by a distance equal to the log of the designated contrast ratio. This gives the hiding power in square feet per gallon. A convenient method is to spray a good many tared clear glass slides with increasing amounts of the paint, and then, after
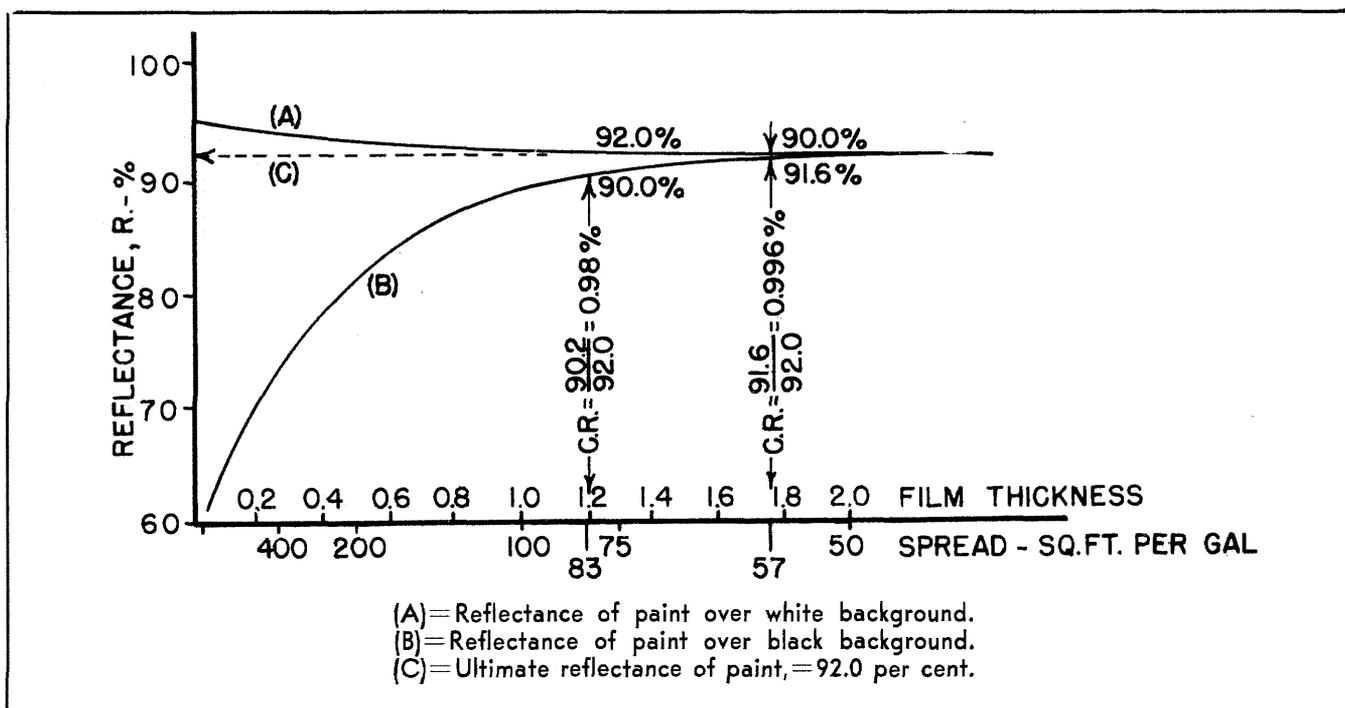
FIG. 4. Reflectance of white paint on black and white bases.

(A) = Reflectance of paint over white background.
(B) = Reflectance of paint over black background.
(C) = Ultimate reflectance of paint, = 92.0 per cent.

drying thoroughly, to weigh them. The spreading rate may then be calculated from the weight of film, the area, the non-volatile content of the paint and its specific gravity. The reflectance of each slide is then measured by placing it first over a white background, then over a black one. The curves are then made as described above.

Another more convenient method than either of the two described above, but less accurate than the photometric method, is the use of the cryptometer. It is a glass plate with pegs at one end so as to form a wedge of the liquid paint when pressed down onto a flat surface. The distance up the wedge to obscure a black and white pattern below is noted. Knowing the slope of the wedge and the distance up the slope, one may read off directly the film thickness and consequently the spreading rate in square feet per gallon. This method suffers the same psychological uncertainty as the visual brush-test. A photometer can be used in connection with the wedge. In this case a straight ribbon filament lamp is used and a sharp image is formed laterally across the movable wedge. The whole wedge assembly can be moved laterally to allow the image to fall first over the black and then over the white section below the wedge. By observing how far up the wedge the filament image lies, one can determine the thickness. The log-reflectances are then plotted against the spreading rate in square feet per gallon as indicated above. Naturally only wet paint can be measured by this method, and there is usually an increase in hiding power when the volatiles leave the film.

The general reflection equation may be modified to give hiding power figures directly, for whites and near-whites. The hiding power is given in square feet per gallon which is secured by solving the reflectance equation for $\frac{1}{x}$ and multiplying by the cubic feet of dry paint in a gallon of liquid paint.

This gives

$$\frac{1}{X} = \frac{r\left(\frac{1}{H_\infty} - H_\infty\right)}{\ln\left[\frac{(\frac{1}{H_\infty} - H)(H' - H_\infty)}{(H_\infty - H)(H' - \frac{1}{H_\infty})}\right]}$$

If we substitute the value of the Fechner fraction F, for

$$\frac{H_\infty - H}{H_\infty}$$

and let the background be black, $H' = O$, the equation reduces to hiding power

$$\frac{1}{X} = \frac{r\left(\frac{1}{H_\infty} - H_\infty\right)}{\ln\left[\frac{1 - (1 - F)H_\infty^2}{F}\right]}$$

Here we see that all-important principle that the hiding power of a white paint is a function of its ultimate brightness, or whiteness. For the ideally pure white, where $s = o$, the hiding power would be extremely poor. To demonstrate the great effect on hiding power of adding a small amount of black to the white paint to reduce its brightness, a curve is presented in *Fig.* 5 which is based on a Fechner fraction of 0.004; such as when the black background has been lightened up to within 0.4 per cent of the ultimate brightness, the surface is called completely hidden.

Thus the hiding power of one of the whitest paints it is possible to make with present raw materials can be increased 50 per cent simply by adding enough black to reduce the relative brightness from 93 per cent to 80 per cent. The latter brightness would still be called

Pigment	Index of Refraction	$*\left(\dfrac{n-1.50}{n+1.50}\right)^2$	Hiding Power, Approx. Sq. Ft./Lb.
Silica, SiO_2	1.55	0.0003	
Whiting, Calcium Carbonate	1.60	0.001	1
Basic Sulfate white lead	1.93	0.015	14
Basic Carbonate white lead	1.95	0.017	23
Zinc Oxide	2.02	0.022	28
Antimony Oxide	2.20	0.036	30
Zinc Sulfide	2.37	0.051	45
Titanium Oxide, TiO_2			
Anatase Crystal System	2.55	0.068	65
Rutile Crystal System	2.76	0.087	80

* Average Vehicle index = 1.50

a good white—about the same as average white paper. Actually the tinted paint often appears whiter because it is possible thereby to correct the slight yellow cast which is always present in the brightest enamels. All common white pigments have a slight absorption in the blue end of the spectrum and most vehicles exaggerate this defect. Since in correcting this absorption we are not at liberty to increase reflectance. we must add a complementary shade to pull the whole visual reflectance down to the minimum value in the blue end. The remarkable economy in reduced pigment content of such controlled paints is apparent from the curve in *Fig. 5.*

In connection with the physical significance of the term *r*, the coefficient of remission or scattering. it might be emphasized that this constant gets its value primarily from the relative index of refraction of the pigment and the vehicle. The 90-degree reflection formula of Fresnel's gives a semi-quantitative measure of the pigment's hiding power, since it contributes to the two principal phenomena of reflection and refraction. The true Raleigh scattering effect does not contribute much. since the particle size of a properly prepared pigment is above that required for this effect. Table No. I will give a quick answer to the question of why the titanium oxide industry grew up in such a hurry!

In connection with the hiding power question an interesting case came out of the infrared camouflage paint development. As is well known now. the greens made from Prussian blue and yellow photograph much darker in the near infrared region (7000-9000 Å) than does green foliage of the same visual green shade. To overcome this it is common practice to replace the Prussian blue with ultramarine blue. or. better still. with copper phthalocyanine blue. which does not have the sharp infrared absorption band that Prussian blue has.

Infrared reflectance tests were made by photographing. on infrared plates. the test-panels. which were simply brushed out to give good visual hiding power. Persistent discrepancies between testing agencies finally indicated that. although the hiding power of the visual color was fully complete, in the infrared it was far from complete.

If the hiding power equation given above is referred to. it will be noticed that the coefficient of remission is in the numerator. Now this constant is largely dependent upon the relative difference in index of refraction between the pigment and the vehicle. since that is the contributing factor in its refractive powers. Since indexes of refraction become less with increasing wavelength. the net result is a great reduction in the value

of *r* as the wave-length increases. roughly in proportion to the change in the function

$$\left[\frac{n_p - n_v}{n_p + n_v}\right]^2$$

where n_p and n_r are in the indexes of refraction of pigment and vehicle respectively.

Since the value of the ultimate brightness was made roughly constant by use of the proper pigments. the net result is an indicated decrease in infrared hiding power. This is the converse of the case mentioned in connection with the ultimate brightness-hiding power relation. where *r* remained constant and the coefficient of absorption was increased by adding black. thereby greatly increasing hiding power.

The use of the equation is in no way restricted to colorless pigments. since the assumptions made as to light-scattering and absorption hold over any band as long as the light intensity is constant over its width. Colored pigments are the same as blacks and whites. except that the coefficient of absorption. *s*. varies rapidly as the wave-length changes. The only new problems involved are in the choice of the wave-length for measurement and in the value of the Fechner fraction for that wave-length band. Neither of these two questions has been settled as yet. and measurements at present are being made just as in the case of black and white. that is. over the whole visual spectrum.
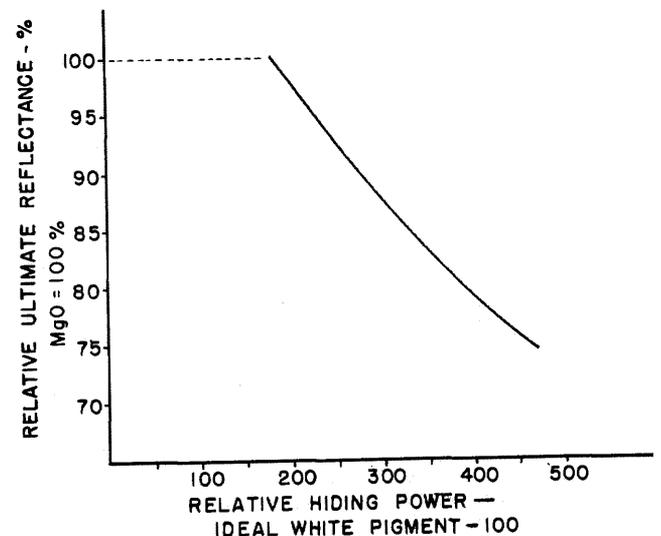

FIG. 5.