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# Conservation: Hearings, Reports (1966-1973): Article 01

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# COLOR CHANGE IN OIL PAINTINGS

ROBERT L. FELLER

**D**URING a recent meeting at a prominent art gallery in New York a collector asked the author to examine a painting by a young artist with whom he was acquainted. His remarks ran something like this: "The gallery purchased this picture before the war. Some of the colors in it, particularly areas of blue and purple, have now discolored so badly that I'm afraid the picture is lost. I believe the artist used to mix alizarin and certain other pigments together to obtain a favorite color. As I recall, such mixtures are not permanent." That afternoon the staff conservator and the author studied the painting. We found the principal difficulty was not that the pigments had altered, but that the surface varnish had failed in an uncommon manner. We therefore suggested that the old varnish be removed and that the picture be revarnished.

The collector's immediate concern about the pigments is a frequently encountered attitude. Color in paintings is, of course, largely due to the pigments. Yet one must not hastily conclude that, because there is an alteration in color, the pigments must have changed. Such faulty reasoning is more prevalent among painters and collectors of twentieth-century art than is warranted. This article will review several causes of color change that do not involve alteration of the pigments. For simplicity the remarks will be restricted to paintings in oil.

It must be admitted that certain pigments used in the past have not proved very durable. But the majority of them are well understood today, and a trained technician can determine if they have been used in a particular picture. In contrast to past history, the contemporary artist has at his command more than forty-

five tested and approved pigments, according to a list prepared by the National Bureau of Standards.<sup>1</sup> The facts concerning these pigments were established over ten years ago through the co-operative efforts of the Bureau of Standards, leading manufacturers, and interested authorities. Nevertheless, artists still occasionally raise questions concerning the durability of their present palette based on these pigments. In closing, the article will discuss several of the most frequently raised questions, such as the one mentioned concerning alizarin.

## COLOR CHANGE OWING TO YELLOWING OF VARNISH AND VEHICLE

A paint consists of pigment and vehicle, and the surface of a painting is usually protected by a coat of picture varnish. Accordingly, light striking a picture often must pass through three components: protective varnish, vehicle, and pigment. It is the influence of the varnish and vehicle upon color to which attention must be directed.

Perhaps the most profound distortion of appearance in paintings is due to the discoloration of natural-resin varnishes. This change may take place gradually over several decades. Often its full extent cannot be appreciated unless one sees areas of the picture with old varnish side by side with areas from which it has been removed. Much has been

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Dr. Feller is the National Gallery of Art fellow at Mellon Institute and is a member of the standing committee on artists' oil paints, Commercial Standard CS98-42. The fellowship, sponsored by the National Gallery of Art, Washington, D. C., is investigating the permanence of artists' materials to develop new materials and techniques, both for original works and for the conservation of museum objects.



DISCOLORATION DUE TO AGED VARNISH CONTRASTS WITH AREAS FROM WHICH IT HAS BEEN REMOVED

written on this subject; it need only be mentioned here. Fortunately old varnish generally can be removed. Moreover, perhaps this problem will become less important in the future, for new varnishes are being introduced, formulated with synthetic resins that have little tendency to yellow. Several museums in this country have over ten years' experience with varnishes of this type.

While discoloration due to varnish often can be repaired, possibly little can be done to rectify yellowing of the medium once it has occurred. This is an important cause of discoloration, but its role should not be overestimated. To demonstrate this point, take a very dark medium, perhaps a copal varnish, and grind pigment in it to make a pastelike paint. In spite of the intense discoloration of the vehicle, the color of the paint usually is reasonably satisfactory. The explanation for this is that the coating of vehicle about each particle of pigment is not sufficiently great to

alter the hue radically.

There are factors other than discoloration, such as the change in refractive index discussed below, or perhaps a separation of the vehicle toward the surface, which must be taken into consideration to account fully for the influence of the aged vehicle upon color. The relative importance of each factor is still open to question and can only be answered when more precise information is at hand. An important step would be the direct measurement of color in paintings. The National Gallery in London has recently described a Lovibond Tintometer adapted especially for this purpose.

The influence of yellowing of the vehicle upon color has been considered by A. P. Laurie in one of his well-known books.<sup>2</sup> He prepared a chart of pigments, summarizing the observations that reds are least affected, then follow yellows, greens, and blues in that order. The diagram on the next page illustrates this information more technically.<sup>3</sup> The arrows indicate how blue, green, and red are "shifted" decreasingly in color when the reflected light must also pass through a yellow filter, "f." The filter, although hypothetical in this example, is similar to the characteristic color of saffron. The location of the slight alteration of the red color is determined by taking into account the fall in sensitivity of the eye (dotted line) in this region. Reflectance curves, such as those used in this diagram, and related data on artists' pigments are available to those interested.<sup>1,4</sup>

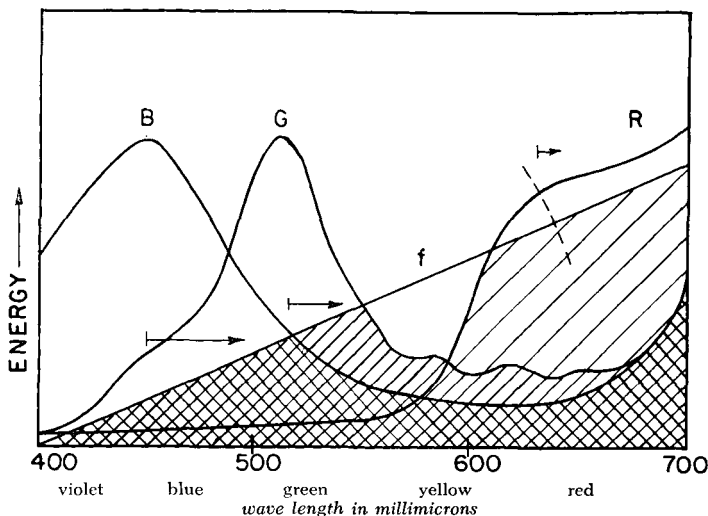
#### COLOR CHANGE OWING TO INCREASING REFRACTIVE INDEX OF OIL

The refractive index of a substance is the ratio of the velocity of light in a vacuum, or, what is very nearly the same, its velocity in air, to the velocity in the substance. The higher the refractive index, the more sharply light will be bent upon entering a medium

from one of low refractive index, and the more light that will be reflected at its surface, or at the "interface." What does this mean in practical experience? For example: if a colorless mineral is immersed in a liquid of the same index, light will travel at the same rate in the liquid and in the mineral. As a consequence, the ray will not be deflected at the surface of the mineral particle, and the particle cannot be seen! Powdered glass (refractive index,  $n_D = 1.5$ ) is white in air ( $n_D = 1.0$ ) because of the diffuse surface-reflection; but when immersed in water ( $n_D = 1.3$ ) or benzene ( $n_D = 1.5$ ) it can scarcely be detected.

That the refractive index of the medium exerts a marked effect on color may be demonstrated simply by placing a pigment in a series of vials containing water, petroleum ( $n_D = 1.4$ ), turpentine ( $n_D = 1.47$ ), and benzene. Generally the color will appear darker as the refractive index increases. This effect is largely responsible for the striking changes which occur when a pastel painting is heavily sprayed with fixative. In another familiar example, the index of refraction of alumina ( $n_D = 1.5$  to  $1.6$ ), in lakes of alizarin and phthalocyanine colors, is nearly the same as that of oil ( $n_D = 1.48$  to  $1.50$ ); these paints form transparent glazes, whereas paints of titanium dioxide ( $n_D = 2.5$  to  $2.6$ ) and vermilion ( $n_D = 2.8$  to  $3.1$ ) are opaque. The high index of titanium dioxide causes the pigment to reflect a considerable proportion of the incident light, making this white one of remarkable "covering power" and brilliance.

Linseed oil increases in refractive index with age. This is because the oxidation and con-



EFFECT OF YELLOW FILTER UPON COLOR REFLECTED FROM BLUE, GREEN, AND RED PIGMENTS

densation of the simple oils, leading to the formation of the tough linoxyn film, involves the gradual formation of a substance having a different index of refraction, as well as other "new" physical properties. Laurie<sup>5</sup> investigated this change and reported that linseed oil varies from an index of 1.48, in fresh oil, to 1.60, in five- or six-hundred-year old objects. His studies of authenticated paintings showed a regular change with age. He even suggested that this phenomenon be used as a means of dating oil paintings. The lower refractive index in fresh oil may be compared to air in the example of powdered glass. As the refractive index of the oil increases, a paint more nearly approaches the example of powdered glass in water. Refractive index influences transparency in paints and, as a consequence, color.

The most dramatic occurrences of this change in oil paintings are the examples of "pentimenti," under-painting showing through in time. The de Hooch *Interior of a Dutch House* at the National Gallery, London, is a well-known case. In this three-hundred-year-old painting, the checkerboard pattern

in the floor is now disclosed through the lady's skirt. The artist evidently painted the figure over the floor pattern, thinking the pattern well covered up, but the paint has become more transparent in the passage of years. Colors, as well as shapes, may eventually show through in this manner. The fault, however, is not due to changes in the pigments.

The alteration of color owing to a change in the refractive index of the medium is inherent in vehicles that undergo extensive oxidation, or polymerization, as do our "drying oils." It is not a major phenomenon in beeswax or glue, for example. This problem, together with that of yellowing, has been discussed by Laurie in *The Painter's Methods and Materials*, chapter IX. The phenomenon receives most attention, however, in regard to pentimenti.

Should artists continue to use polymerizable mediums, with their advantage of becoming relatively insoluble in time, the alteration of refractive index might be speeded up by baking, as is done with modern industrial finishes. The forger, Van Meegeren, constructed an oven and used a modern resin in this manner, although for other reasons.<sup>6</sup>

#### COLOR CHANGE DUE TO SURFACE OF VARNISH OR UNEVEN CLEANING

If a varnish has a mat finish, the color beneath will not be as intense as it might be; it will be "hazy" because of the diffused surface-reflection. The varnish surface therefore influences the "total effect" of the picture. Similarly, uneven removal of discolored varnish will alter the appearance. This fact is very important in museums, where the appearance of the picture is controlled by the processes of conservation and cleaning, on those occasions when it is found necessary and advisable to treat the painting in the laboratory. There is on record, for example,

that old varnish lies over the gold ornaments and decorations in Velazquez's portrait of *Philip IV when Elderly*.<sup>7</sup> In another case, Brandi<sup>8</sup> mentions that the background of the *Pieta* of Sebastiano del Piombo was less prominent than originally intended because of a tinted "beverone" (wash) over the landscape. A connoisseur may comment on these affects without realizing that it is uneven cleaning (and not the pigments) which is at fault.

#### COLOR CHANGE OWING TO CHANGE IN ILLUMINATING LIGHT

The illuminating light, whether daylight, an incandescent lamp, or a fluorescent lamp, may alter considerably the color seen by an observer. The light from an incandescent lamp resembles the characteristic curve of filter "f" in the diagram. Compared to a north light, there is a deficiency in the shorter wave lengths. Little "blue" is present for the eye to see, even though pigments are present that reflect light of this wave length. Painters who paint under lamps at night are often quite impressed with this fact. Since pictures may be exhibited under different conditions of illumination, this factor should not be overlooked when criticizing "alterations of color."

#### COLOR CHANGE OWING TO CHEMICAL CHANGES IN THE PIGMENTS

Thus far the several changes discussed have not involved alteration of the pigments. While it is true that certain pigments of the past have changed, the factors mentioned must not be underestimated. If discoloration can be shown not to be due to the above causes, then one may test to see if pigments known to be fugitive are present. This can be done with considerable accuracy, but in the last analysis it necessitates technical examination by an expert.

At present it is appropriate to restrict this discussion to the list of "permanent" pigments specified in the Bureau of Standards report.<sup>1</sup> Artists should have high confidence in this palette, and be grateful to the manufacturers and technical advisers who established these standards. The primary test of durability, or admissibility, to this list is based on light fastness during out-of-door exposure. Certain pigments that do not appear on this list may be just as permanent, but the artist should make a special point to check.

Other than fastness to light, of which there is little doubt, artists still speak occasionally of the incompatibility of certain pigments. By this is meant a chemical reaction between two pigments when mixed together. It is not widely known, but Gettens<sup>9</sup> several years ago directed a special study of this very problem. The experiments involved white lead, sulfides, chromates, copper salts, and alizarin. Under severe conditions of light, humidity, and temperature, copper and chromate pigments reacted much as expected. These particular pigments are not in the Bureau of Standards list. In all other cases of suspected incompatibility, the linseed oil evidently protected the particles sufficiently to prevent chemical reaction.

The recommendation by Fischer,<sup>10</sup> that alizarin not be mixed with earth pigments, was not found necessary as a result of these experiments. Fischer's suggestion was based on the fact that different earths are sometimes used to modify the shade of alizarin lakes during manufacture. He therefore recommended that alizarin not be mixed with certain earth pigments. He did not claim that such a mixture was known to be impermanent; he merely suggested that it might be safer not to mix these pigments. Several prominent manufacturers of artists supplies kindly informed the author, during the preparation of this article, that they had not in their experience

found modern alizarin to be incompatible. Testing this possibility under accelerated-aging conditions is not easy, however. Nevertheless, such tests lead to the conclusion that oil paints containing copper and chromate pigments represent the principal cases where instability can be demonstrated.

In conclusion, it must be emphasized that one must not be hasty to attribute color change to fugitive or incompatible pigments. This statement is particularly true regarding the oil paints listed in CS98-42.<sup>1</sup> An artist reading literature concerning durability must carefully consider the date of the publication of information referred to. Writers occasionally quote Doerner, Toch, and others on matters concerning which there are more modern data. There is still much to learn about the behavior of pigments; nevertheless, present manufacturers are able to supply the artist with more carefully prepared colors than were available in years past. They also are able to base their judgment on technical publications and special reports such as Commercial Standard CS98-42 and the work of Gettens and Sterner, data not widely known to artists. The author wishes to call particular attention to these two publications and to the fundamental phenomenon of the change in the refractive index of oil.

#### LITERATURE REFERENCES

<sup>1</sup> "Artists' Oil Paints," Commercial Standard CS98-42, United States Government Printing Office, Washington, D. C., 1942. Price: Five Cents, Superintendent of Documents, Washington, D. C. Reprinted: Ralph Mayer, *The Artists Handbook of Materials and Techniques*. The Viking Press, New York, 1948, p. 519.

<sup>2</sup> A. P. Laurie, *The Painter's Methods and Materials*, J. B. Lippincott Company, Philadelphia, 1926, p. 124.

<sup>3</sup> For a more complete discussion of color and a graphical representation of color, see Ralph M. Evans, *An Introduction to Color*, John Wiley & Sons, N. Y., 1948.

<sup>4</sup> N. F. Barnes, *J. Opt. Soc. Am.*, **29**, 208 (1939).

<sup>5</sup> A. P. Laurie, Proc. Royal Soc. London, **159**, 123 (1937); Trans. Faraday Soc., **33** (2), 393 (1937).

<sup>6</sup> P. Coremans, *Van Meegeren's Faked Vermeers and deHooghs*, Cassell & Co. Ltd., London, 1949, p. 20.

<sup>7</sup> Weaver Report, Museum, **3**, 129 (1950). Reprinted in *The Care of Paintings*, UNESCO, represented by Columbia University Press, N. Y.

<sup>8</sup> C. Brandi, Museum, **3**, 208 (1950). Reprinted as in 7.

<sup>9</sup> R. J. Gettens and F. W. Sterner, *Technical Studies in the Field of Fine Arts*, **10**, 18 (1941-42).

<sup>10</sup> M. Fischer, *The Permanent Palette*, National Publishing Society, Mountain Lake Park, Md., 1930.

#### AUTHOR'S NOTE

The principal intent in this review was to draw attention to factors in color change which do not involve alteration of the pigments. No attempt was made to treat adequately the subject of chemical change involving pigments. Lack of emphasis in this regard was not intended to imply minor importance, although it is perhaps of less importance in the palette of the contemporary artist than was the case in the past.

The reaction of pigments with other pig-

ments, the subject of incompatibility, was mentioned as being perhaps of less significance than once thought. The reaction of pigments with the vehicle should also have been mentioned, because it is in a sense unavoidable. The formation of soaps in the linseed oil by reaction with white lead and by zinc white, for example, may also offer certain advantages, such as increased toughness and durability of the paint, which must be balanced against the disadvantages. Decomposition, rearrangement of structure, and reactions of pigments with outside agents (such as water vapor, oxygen, and atmospheric contaminants) are the changes most generally considered in discussing undesirable failure to pigments. This subject was omitted, even the most obvious examples, owing to limitations of space.

Light and heat, of course, are not considered as reactants, but as agencies which may accelerate any of the forementioned changes.

—R. L. F.

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