THE PERMANENCY OF PAINTINGS[1]

BY WILDER D. BANCROFT

When light is absorbed by a substance, the substance tends to change and consequently there is a tendency for light to affect all pigments. Since the light produces but a relatively small change in the chemical energy, it depends on the special conditions whether any given pigment is affected or not. There is no particular type of reaction produced by light of any given wave-length. It is not true, for instance, that the blue rays have a reducing action and the red rays an oxidizing action. Light may cause or accelerate an oxidation, a reduction, an allotropic change, a dissociation, a condensation, or a metathetical reaction. The change that takes place depends entirely on the chemical conditions prevailing while the pigment is exposed to light. Methylene blue, for instance, may fade as a result of reduction[2] or of oxidation. The bleaching of methylene blue is usually an oxidation because of the oxygen in the air. In presence of gelatine[3] or of stronger reducing agents the bleaching of methylene blue by light is due to a reduction. On standing in the dark the leuco base is oxidized and the color comes back.

In the case of water colors, the change due to light is usually an oxidation. It seems possible that the rapid fading of water colors may be due in part to the gum[4] acting as an oxygen carrier. This should be looked into, because it might be possible to use some substitute for gum which would not produce such harmful results.

With oil paints we may get a reduction in case the oil contains a drier. The drier acts as an oxygen carrier to oxidize the oil. In addition to taking oxygen from the air, it may re-

[1] A paper read before the Eighth International Congress of Applied Chemistry in New York, September, 1912.
[2] Cf. Wander: Jour. Chem. Soc., 66, II, 122 (1894).
[3] Gebhard: Zeit. phys. Chem., 79, 639 (1912).
[4] Cf. Struve: Liebig's Ann., 163, 160 (1872).

duce the pigment, especially if the supply of oxygen be limited. We get an admirable instance of this with Prussian blue.[1] "When Prussian blue or any of its analogues are mixed with white lead or flake white, the rich sky blue or greenish tint, which will result, bleaches over night into a sickly green; but, on exposure to the light for an hour, it comes back to its original color."

Here the white lead acts to a certain extent as a drier. Under some conditions a slight reduction of ferric oxide takes place.[2] "Upon long and extreme exposure the bright Indian red loses its brilliancy and turns darker, which is due to the chemical change or decomposition from the ferric to the ferrous state. The ferrous [ferro-ferric] oxide of iron is a black oxide with which the artistic painter is not acquainted. The ferric oxide of iron is the bright, red oxide. The darkening effect of Indian red is due to the slight change from the ferric to the ferrous [ferro-ferric] oxide. The same is true when Indian red is mixed with zinc oxide to produce a flesh tint. The author exposed a sample so made for three years to the bright daylight, and at the end of three years a very slight darkening had taken place; but, inasmuch as artistic paintings are rarely, if ever, exposed to the bright sunshine throughout the entire year, Indian red must be regarded as one of the permanent and reliable pigments." Toch[3] also states that "driers decompose many pigments. In fact, nearly every one of the lake colors is rapidly affected by the action of driers. Madder lake, when mixed with a lead or manganese drier soon loses its pristine brilliancy." In presence of oxygen the drier oxidizes the pigment. In presence of oil and only a slight amount of oxygen, the drier reduces the pigment and oxidizes the oil.

With vermilion we have an allotropic change from the red form to the black. It appears to take place more readily

[1] Toch: Materials for Permanent Painting, 152 (1911).

[2] Toch: Ibid., 132 (1911).

[3] Materials for Permanent Painting, 75 (1911).

in water colors[1] than in oils. "In water-color painting most vermilions are found to be changed on exposure, the solar rays gradually converting the red into the black modification of mercuric sulphide, without, of course, producing any chemical alteration. This change occurs even in the absence of air and of moisture. Impure air, *per se*, even if sulphuretted hydrogen be present, does not discolor vermilion.

"Anyone who has examined old illuminated manuscripts must have noticed the apparent capriciousness with which the ornaments, and especially the initial letters, painted with vermilion, have been affected. I have more than once observed that, while all the vermilion used in one part of a missal or choral-book has remained red, a leaden hue has spread irregularly over the rest of the work in places where this pigment has been used. This may be due to the use by the illuminator of a sample of vermilion adulterated with minium or red lead, but sometimes to a change in the technique, as a change in the style or handiwork is often associated with the difference above described. In oil-painting there are no permanent pigments, save the copper-greens, with which vermilion may not be safely mixed. Only when it contains impurities, such as free sulphur, does it darken flake-white.

"Vermilion prepared from native cinnabar is found perfectly preserved in the flesh-tints of Italian tempera-paintings of the thirteenth and fourteenth and fifteenth centuries. It has stood in the wall-paintings of Pompeii, where it often seems to have been waxed. A comparatively recent but instructive instance of the permanence of vermilion in oil is furnished by a portrait, dated 1758, in the National Museum Gallery. It represents the painter, Hogarth, with his palette set before him. The second of the dabs of color thereon is vermilion, perfectly intact. In the same collection there is a portrait by Marc Gheeraedts of Mary Sidney, Countess of Pembroke, in which the vermilion has stood. This work was painted in 1614. Scores of earlier and later examples might

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[1] Church: The Chemistry of Paints and Painting, third edition, 169 (1901).

be cited." Since the discoloring of vermilion is an allotropic change and is therefore independent of other reagents, it might seem as though vermilion ought always to be stable or always to be instable. I shall take this point up later when considering methods of preventing the light from changing pigments.

The case of carmine presents certain difficulties. There is no question but that carmine is instable in light. Church[1] says that "beautiful and rich as are the colors prepared from cochineal, not one of them should ever find a place upon the palette of the artist. They all become brownish, and ultimately almost disappear after a short exposure to sunlight or the more prolonged attack of strong diffused daylight. In six hours of sunshine a strong wash of fine crimson lake on Whatman paper lost 8 percent of its original intensity; this was on April 12. The loss during a second period of six hours' exposure was much less, but after the lapse of four months less than 5 percent of the original color remained. In the case of carmine, from one to two years was required for the complete obliteration of every trace of the original crimson from a deep wash of this pigment. All the cochineal pigments become somewhat brownish during the course of fading, but ultimately, when all the red has disappeared, either a greenish grey or a faint sepia-like brown is the sole residue."

Notwithstanding this evidence as to the instability of carmine there exists a tradition that a first-class grade of carmine can only be made in sunlight.[2] Never having seen carmine made, I do not know whether this belief is erroneous or what the explanation is in case the belief is true. The only guess which occurs to me is that the raw carmine contains some impurity which is more readily destroyed by sunlight than the carmine itself.

The permanency of pigments in light is complicated by

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[1] The Chemistry of Paints and Painting, third edition, 186 (1901).
[2] Bersch: Manufacture of Mineral and Lake Pigments, 358 (1901).

the presence of gases in the atmosphere.[1] "In all large communities there exists sulphuric acid in the air, and many colors which we have regarded as permanent to light, are not permanent to the effect of acid gases. In a general way this rule applies also to the colors affected by sulphuretted hydrogen. If we take, for instance, red lead, which is the red oxide of lead, and expose it to the air of a city it apparently bleaches white. The same red lead when varnished and covered with glass may be exposed for ages and will not be affected. We note the former change particularly on steel structures like bridges, which have been painted with red lead and on which the color sometimes bleaches from a pure scarlet to a pale pink. On rubbing such a surface with linseed oil and turpentine the original color comes back in all its brilliancy. Upon investigation, we find that the sulphuric acid and red lead formed a minute crystalline surface of sulphate of lead, which is white. Chrome yellow will be affected in the same way. Improperly washed Prussian blue will likewise bleach, and flake white is affected in identically the same manner, with the exception, that the change cannot be noted by the eye, but if a flake white surface, which has been exposed to the elements, is rubbed with a black cloth, a white chalky deposit will stain the cloth. This is known as chalking, and mural decorations which cannot very well be varnished and protected, should therefore be executed with pigments that are not affected by the acid gases of sulphur. Nearly all the pigments are affected, with the exception of the blacks. The ochres, siennas and the earth colors, which are exceedingly permanent, show this defect although to a less degree as compared with the chemical colors like Prussian blue, the lakes, cadmium yellow and the lead colors; but paintings which are kept in a pure atmosphere under glass are necessarily preserved, and water colors are more susceptible than any other form of painting."

The blackening of white lead by hydrogen sulphide can

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[1] Toch: Materials of Permanent Painting, 181 (1911).

be counteracted to some extent by exposing the lead sulphide to ight and air, in which case it is oxidized to lead sulphate.[1]

'My attention was directed to the action of light upon the sulphide of lead from observing that in the glass cases in the Technological Museum under my charge at the Crystal Palace, which are painted white with white lead, substances which emitted sulphurous vapors did not cause a darkening of the surface of the case, except where it was protected from the direct influence of light.

"In the case devoted to sulphur, for instance, the spaces obscur.d by th descriptive cards alone were blackened, the white color of the rest of the case being unimpaired. In the cases containing vulcanized rubber, wools, woolen fabrics, hair, and other animal products containing sulphur, the same appearances were presented.

"In the first-named of these cases I had placed the dried leaves of the gutta-percha plant, attached to a piece of cartridge paper—a translucent substance. Upon removing the paper I found a tolerably faithful photograph of the leaves upon the surface of the case.

"In order to verify these observations, and to gain a knowledge of the cause and rapidity of the action, and at the same time to ascertain the effect of the colored rays upon sulphide of lead, the following experiments were made:

"A board painted white with white lead and oil was exposed in a chamber for several hours to the action of sulphide of hydrogen gas until the painted surface had acquired a nearly uniform chocolate or deep-brown hue. Plates of glass of different colors were then placed upon the painted surface, one portion being at the same time covered by an opaque medium, and another left open and unveiled to the light. The board was then placed in a situation facing the east.

"'The glasses which I employed were of the following colors and properties: 1, red; 2, blue; 3, yellow; 4, violet; 5, a glass that diminishes the intensity of all the rays; and 6,

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[1] Price: Jour. Chem. Soc., **18**, 245 (1865).

a glass which slightly reduces the yellow ray.   My friend, Mr.
Robert Hunt, F.R.S., was kind enough to lend me the series
of colored glasses which he employed in his investigations,
for the British Association, and the optical properties of
which he had determined; but, with the above exceptions, I
have not thought it requisite to record the results obtained,
desiring rather to v'ew he subject from a practical point.
The results shown are from an exposure of eight days, on one
of which only was the atmosphere clouded.   It will be ob-
served that the surface exposed to the action of light is now
perfectly white, while that under the influence of the red ray re-
mained as dark as where the sulphide had been protected from
light.   The blue ray has effected an almost complete conver-
sion of the sulphide; the yellow ray a partial, and the violet
considerably less action than the yellow.   The light passing
through glass 5 has produced somewhat less effect than has
resulted from the blue rays, while with glass 6 the action has
been nearly as rapid as where the surface has been left quite
exposed to the light.   The action of drying oils is very rapid
upon sulphide of lead, an exposure to light for a few days,
only being sufficient to change a surface of it coated with a
thin layer of linseed oil into a white one.   When boiled lin-
seed oil is used, still less time is required to effect the change.
That the action is an oxidizing one there can, therefore, be
little doubt, and I regret that I have not been able to get the
further proofs on this point ready for this occasion, but know-
ing that there are many in Birmingham who might be inter-
ested in the subject, I have thought it better not to defer the
communication of these results on that account.   It is, how-
ever, not only when mixed with oil that the conversion of the
sulphide is accomplished, for where water color was used, the
action was still marked, although slow, as will be seen by
the illustration exhibited in which the dark spaces were pro-
tected from the light by cards and other opaque substances.

   "These observations serve to explain part of the evidence
given before the 'Royal Commission appointed in 1857 to re-
port upon the site best adapted for the National Gallery,

in reference to the facts stated by directors of galleries, artists and picture dealers, as to the injury which pictures suffer by being kept in ill-ventilated and badly lighted places, and of the beneficial effects resulting, in many instances, from the exposure to direct sunlight of injured pictures.

"From this report I quote the following: Mr. Knight, the Secretary of the Royal Academy, stated that he preferred pictures to be exposed to the light if he wanted to preserve the lights of a picture. Mr. Farrer mentioned a case where, by exposing a picture that had been kept in the dark, the blue became brighter. Sir Charles Eastlake, P.R.A., instanced the case of some of the pictures from the late Mr. Turner's gallery, those of 'the Deluge' and 'Queen Mab' in particular, where the whites were turned into blacks, and stated that white lead, if not tolerably well secured from the effects of the atmosphere, would undergo a rapid change in London, and that it was a very general opinion that pictures look better and last longer in the country than in London. Mr. Bentley, who restored these pictures by a secret and chemical process, said that the highest light was perfectly black and that, in fact, 'high light' was 'high dark.'

"I have here an illustration to show that the changes effected by the secret and chemical process may be brought about by simple exposure of the picture to the light. The picture was placed in an atmosphere of sulphide of hydrogen gas until it had acquired a dark brown color. Strips of paper were then fastened across parts of the surface, and it was placed in a window facing the light. Those portions not obscured, it will be observed, have resumed their original appearance, while those covered by the paper remain as black as when the paper was first placed over them.

"Mr. Cooke, R.A., stated that light is one of the greatest agents in the preservation of pictures; that it helps to develop them in every way, particularly with regard to the varnish, and he gave an instance of a picture of his own which he had lent for exhibition to a gallery where it had been exposed to a very strong light; that five months afterwards,

when it was returned to him, he was surprised at its extremely bright appearance. .

"In reference to the action of light on varnish mentioned by Mr. Cooke, I may observe that I have found that when light is excluded from a painted white surface, the surface assumes a dingy yellow color, but that the original color is restored by admitting the light to it. This fact is, I find from the report, acknowledged by many artists.

"I have said that the glass cases containing woolen fabrics were blackened, and it may be well to draw attention again to the fact, with a view of showing that no small source of sulphur vapor in the atmosphere of a gallery frequented as the galleries in London are, may arise from the clothes of the visitors."

"That the experiments which I have described, taken in conjunction with the testimony just read, have an important bearing upon the preservation of paintings, will, I think, be evident, as they demonstrate the protecting influence of light upon white lead and those colors with which it is mixed, where the atmosphere is or may become contaminated with sulphurous gases, and conversely the deterioration that paintings must suffer where under the same circumstances the light admitted is feeble—facts deserving of attention in the construction of galleries in the metropolis and large manufacturing towns, and by those who have the care of paintings in churches and public buildings, or who possess collections of their own, and adopt the practice of covering their pictures.

"It is curious to observe in many parts of London the discoloration of houses painted with white lead. I have frequently seen the lower portions completely coated with a metallic-like surface of the sulphide, and I have little doubt that the formation of this compound will be found to be more frequent in winter than in summer time, and more prevalent on the shady than on the sunny side of a street."

The secret chemical process referred to by Price undoubtedly consisted in the use of an oxidizing agent. Hydrogen peroxide is the substance usually recommended for this

purpose; but there is no reason why we should be limited to this oxidizing agent and, as a matter of fact, any oxidizing agent may do more harm than good[1] in certain cases.

"Where sulphur fumes have decomposed the lead color and formed a brownish result, chemists have recommended the use of peroxide of hydrogen, and while this may be theoretically the proper method to pursue, it is not necessary, and sometimes dangerous, for the reason that even though peroxide of hydrogen will bring back flake white and chrome yellow to their original color, it may bleach an adjacent lake beyond redemption, and as these sulphur decompositions of color are usually on the surface, the wood alcohol and turpentine treatment with very slight abrasion, will produce all the results necessary. The cleaning and renovation of pictures in the hands of an intelligent person is not a very difficult problem, but it is very easy to spoil any good painting by the use of nostrums and recipes which are destructive in their effect."

"A 'secret chemical process' which works well in some cases is to take soap and water, and to wash off the extremely thin film of discolored pigment. The simplest way to prevent the formation of lead sulphide is not to use a color containing lead. On the painter's palette, flake white has been practically superseded by Chinese white; but the less dangerous lemon yellow is still used.

"The effects due to harmful gases in the air and to a varying dewpoint can be minimized by keeping paintings carefully varnished and by painting the back of the canvas.[2] If the pigments are not washed carefully when they are prepared, substances may be left in which will have a deleterious effect either on that pigment or on some other pigment with which it may later be mixed. This is responsible for some of the contradictory reports in regard to the permanency of certain colors. Aurelian and cadmium yellow are typical cases.[3]

[1] Toch: Materials for Permanent Painting, 61 (1911).
[2] Toch: Ibid., 182 (1911).
[3] Toch: Ibid., 90, 102 (1911).

"Aurelian is a pigment that has been introduced during the last generation, and is sometimes sold under the name of cobalt yellow. It is a double nitrite of cobalt and potassium. There is a variety of opinion as to its permanency. Some claim that it is absolutely permanent both in water and in oil, and others claim that it decomposes with a white, but from the experiments made by the author its permanence depends entirely upon its purity. If the color is thoroughly washed by the manufacturer after it is precipitated in order to free it from soluble salts, it may be regarded as absolutely permanent, because it is not affected by sulphur gases nor by sunlight. If the color is impure, it is very likely to decompose any lake which may be added to it, and when mixed with new linseed oil, it loses its brilliancy in a short time. There are several good manufacturers of this pigment, whose aurelian yellow may be used and regarded as absolutely permanent."

"Cadmium yellow may fail, and in many instances does fail, because it is improperly made and because it is ground in an emulsion of oil and water, or because the oil in which it is ground may be of a highly acid nature. Manufacturers of tube colors ought to learn the lesson that no tube color should be ground in a chemically bleached vegetable oil, for oils are principally bleached by means of a strong acid like sulphuric or chromic, and all traces of these acids are not entirely washed out, so that much trouble may arise from the ultimate effect of this trace of acid, and even a good color like cadmium may be decomposed if the oil be not entirely pure."

We can now consider some possible methods of cutting down the action of light on pigments. While all rays which are absorbed tend to decompose a pigment, the absorbed rays are not equally effective. In the bromination of organic compounds, the most effective rays are those corresponding to the weaker bromine absorption bands in the yellow-green and orange, instead of those corresponding to the stronger absorption bands in the greenish-blue and blue.[1] If we should

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[1] Schramm and Zakrzewski: Monatsheft, 8, 299 (1897).

cover a pigment with some substance which would cut off the more effective rays, we should increase the permanency of that pigment to light very much. Though we have no quantitative spectroscopic study of this point, this case appears to occur with vermilion and madder.[1]

"Vermilion is a sulphide of mercury, and is artificially made by mixing sulphur and mercury in the presence of an alkaline solution under heat and pressure. It ranges in shade from a light orange to a deep scarlet, and while it is perfectly true that when used alone as an oil color and exposed to the brilliant sun rays, it will darken considerably, when glazed over with madder, as is frequently done after it is thoroughly dry, it is remarkably permanent, or when properly varnished it is very stable."

The varnish on a picture cuts off the ultra-violet light to a very great extent and protects the picture in this way, in addition to keeping out moisture and the gases in the air.

The yellowing of pictures is due to a change in the oil.[2] "That the cause is what may be termed the effect of light on a mixture of white lead, zinc oxide and linseed oil, or a linseed oil varnish is evident because paint chemists have long known that white lead in any form, whether it be called flake white, cremnitz white, silver white or white lead, has a reducing action on the pigment present in linseed oil, or linseed oil varnish, and that this reducing action changes this pigment into another pigment which is yellow. It may fairly be asked whether such a reaction can take place if the linseed oil is bleached. To this question the reply must be given that the bleaching of linseed oil does not destroy the color which is present, but simply changes it from an olive yellow to an exceedingly pale yellow, which can hardly be seen, so if we take refined or bleached linseed oil and mix it with white lead or zinc oxide, we have a very brilliant white which remains white as long as it is exposed to bright light. If we

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[1] Toch: Materials for Permanent Paintings, 108 (1911).
[2] Toch: Ibid., **33**, 35, 38 (1911).

take this mixture and place it for six weeks in an absolutely dark place, the white paint changes into the well-known yellow tint and it is this particular change which produces in all paintings the distinct yellowness of age."

"Another line of experiments was carried out, in which bleached linseed oil was also used. This turned exceedingly yellow in three months, but when exposed for three months to the bright sunlight it became brilliant white again, and upon being placed in a dark closet for another three months no change took place. Those parts of the painted experiment which had been bleached by the sunlight remained white in the dark closet at the end of the experiment. This would, therefore, prove that when a picture has turned yellow it can safely be exposed to the sunlight in order to bring back its natural brilliancy, provided, of course, that no part of it has been painted with asphaltum or bitumen, for the asphaltum and bitumen, instead of bleaching in the light, become black."

" If linseed oil is insisted upon by the painter the raw, unbleached, unrefined product should be used, for it is reasonable to assume that it cannot grow any darker as long as the coloring matter is not visibly hidden, but may improve, for upon exposure the color will surely bleach, and upon replacing the painting in a poorly lighted room it will not grow any darker than it originally was when the painter used it."

These experiments raise the question whether a better way of bleaching might not be found which would destroy permanently the coloring matter in the oil.

Since the action of light on pigments is an oxidizing one in the majority of cases, the safest pigments to use are normally those which are made by oxidation and this is a point to be kept in mind when studying coal tar colors. While it is possible that the organic chemist may some day give us a series of colors which are absolutely permanent to light, it will perhaps also be well to consider whether we cannot increase the stability of all or some of the colors that we now have. The coal tar colors are used as pigments chiefly in the form of lakes. In spite of the importance of the matter

we seem to have no definite, quantitative information as to the actual effect due to mordant or to base. In books on dyeing one finds isolated statements that such and such a dye is faster with one particular mordant than with another; but there are no general statements and no attempt at an explanation or theory.

We have found that some lake pigments are more fast to light than the corresponding dye is when dissolved in water; but there is no reason to suppose that this is generally true. Playfair[1] has shown that calcined alumina causes nitric acid to attack indigo. "A portion of alumina may be taken and placed at the bottom of a vessel containing warm $NO_5[HNO_3]$; no action ensues, except partial solution; a strip of calico colored in indigo-blue may now be introduced into the mixture, and remains unaffected in the clear acid, but is immediately discharged when pressed with a glass rod into the alumina. Here the alumina acts by placing the oxygen of the nitric acid in a state of tension without however succeeding in decomposing it, but the moment an assistant affinity comes into play, that state is shown by the decomposition of the nitric acid and the oxidation of the indigo. The alumina in the presence of the acid could not oxidize (in fact we know of no higher oxide), and therefore the indigo appropriates the oxygen. I find that various other oxides, such as calcined Cr_2O_3 and SnO_2 have the same power, the latter showing this disposition more than any of the other oxides."

Of course this experiment of Playfair's does not bear directly on the matter in which we are interested; but it is very suggestive and has an important indirect bearing. In a recent book[2] there is a statement that copper salts are known to increase the stability of all dyes to light. In view of the fact that copper salts act as oxygen carriers, I doubt the accuracy of this statement. It is important either way. If copper salts really do increase the stability of all dyes to light, we must get a theory to account for the fact. If they do not

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[1] Jour. Chem. Soc., 3, 354 (1847).

[2] Limmer: Das Ausbleichverfahren, 43 (1911).

act in this way, the statement serves to illustrate our general ignorance in regard to the subject.

The whole question of double mordants or of fixing agents is also an important one. When we wish fastness to washing we know that we must add lime when we mordant alizarine with alumina. Methylene blue stands soaping if fixed by magnesium and aluminum acetates.[1] Orange No. 2 is fixed by chromium and magnesium acetates; chromium acetate, *per se*, gives a brown color; magnesium acetate *per se* does not fix the color. Grey coupier and induline require chromium or the latter mixed with magnesium acetate.

Of course, fastness to soaping is not the same thing as fastness to light; but the facts are suggestive and open up an unexplored field. Indigo is considered by the dyers as one of the most permanent dyes, while the painters consider it as fugitive.[2] "This transparent blue is unfortunately, gradually oxidized and browned when exposed to light. In thin washes of water-color it disappears rapidly in the sun's rays, much more slowly when submitted to diffused daylight. The following figures approximately represent the reduction in force of a sample of indigo as a moist water-color when exposed to sunlight:

> Original intensity................ 10
> After two years.................. 1
> After ten years.................. 0

Other trials with other samples gave in some cases less unfavorable results. Indigo in cake is sometimes less affected by sunlight than the moist preparations. As an oil-color, indigo loses from one-third to one-half its intensity when exposed to sunlight for five years, its hue being at the same time altered, in different specimens, either to a greyish or a greenish blue; the change is more conspicuous when the indigo has been mixed in tint with flake or other white. Locked

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[1] Koechlichen: Jour. Chem. Soc., **44,** 893 (1883).

[2] Church: The Chemistry of Paints and Painting, third edition, 219 (1901).

up in copal or amber varnish it is more slowly changed. The fading is due to oxidation."

Part of the difference in opinion between dyers and painters is probably due to differences in methods of testing; but I have a suspicion that oriental rugs owe part of their fastness to light to the fact that the weavers did not use chemically pure mordants.

If one wishes to study this subject experimentally, it is desirable to have a method by which tests can be made in a relatively short time. By using different concentrations of peroxides or persulphates we can get oxidizing agents of different strengths in neutral, acid or alkaline solutions. By comparison with dyes which are known to be fast to light we can lay down the arbitrary rule that a pigment is fast to light if there is no appreciable change in a given time in a given solution at a given temperature. Our experiments are only preliminary ones; but the method seems a promising one. There is one interesting thing to be noted. While we should expect to get the same bleaching by light and by the oxidizing agent, the rate of bleaching in the light varies with the relative intensity of the absorbed light and the rates for any two lights are not necessarily equal when the relative intensities of the lights are those necessary to make white light as we see it. As a matter of fact, we found that Victoria green bleached more rapidly than eosine or methylene blue in a hydrogen peroxide solution, while the reverse is the case in sunlight.

There is another point about which we have no theory at present, and that is as to the variation in stability with the method of preparation. Church[1] says that "vermilion prepared from the mineral or native cinnabar is probably less liable to change than the artificial products, whether obtained by the dry way or moist way; but 'moist way' vermilions are certainly the most alterable." The artificial ultramarine is more readily attacked by acids[2] and by alum than is lapis

[1] "The Chemistry of Paints and Painting," third edition, 168 (1901).

[2] Toch: Materials for Permanent Painting, 163 (1911).

lazuli. So far as two samples of vermilion are mercuric sulphide they should behave alike. The difference must therefore be due either to agglomeration or to the presence of adsorbed impurities. In either case it is a problem in colloid chemistry. Our general ignorance in regard to a lot of these things is illustrated by the fact that nobody knows whether lemon chrome and sublimed white lead are or are not definite compounds.

The general results of this paper:

1. Light may change pigments in all sorts of ways; but the change of color is usually due to an oxidation.

2. A drier in the oil may cause reduction of a pigment, the oil being oxidized; or it may accelerate the oxidation of the pigment.

3. Lead sulphide is oxidized to sulphate by light, and pictures which have blackened in the air can therefore be improved by an exposure to bright sunlight.

4. Colors which are really permanent may seem fugitive if prepared improperly or if ground in oil that has been bleached with acid

5. Madder probably protects vermilion by cutting off the rays which are most active in producing the allotropic change.

6. Varnishes keep out moisture air, and ultra-violet light.

7. Pigments produced by oxidation are more likely to be stable than those produced by reduction.

8. By changing the nature of the precipitating agent it ought to be possible to vary the fastness of lakes to light.

9. From the analogy with dyeing, it seems probable that the maximum fastness to light can be obtained when lakes are made with a suitable mixture of precipitating agents.

10. It is doubtful whether copper salts increase the fastness of all dyes to light.

11. Rapid tests for fastness to light can be made with solutions of peroxides or of persulphates.

12. The relation between the stability of vermilion, etc., and the methods of preparation is a problem in colloid chemistry.

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