YELLOW BRICKS

BY L. A. KEANE

In the chapter on the chemical properties of clays, Ries¹ says: "Many clays show a yellow or brown coloration due to the presence of limonite and a red coloration due to hematite; magnetite is rarely present in sufficient quantity to color the clay; siderite or pyrite may color it gray, and it is probable that the green color of many clays is caused by the presence of silicate of iron, this being specially true of glauconitic ones. The intensity of color is not always an indication of the amount of iron present, since the same quantity of iron may, for example, color a sandy clay more intensely than a fine-grained one, provided both are nearly free from carbonaceous matter; the latter, if present in sufficient quantity, may even mask the iron coloration completely. The coloring action will, moreover, be effective only when the iron is evenly distributed through a clay in an extremely fine form. It is probable that the limonite coloring clay is present in an amorphous or non-crystalline form, and forms a coating on the surface of the grains.

"All of the iron ores will in burning change to the red or ferric oxide, provided a sufficient supply of oxygen is able to enter the pores of the clay before it is vitrified; if vitrification occurs, the iron oxide enters into the formation of silicates of complex composition. The color and depth of shade produced by the iron will, however, depend on: first, the amount of iron in the clay; second, the temperature of burning; third, condition of the iron oxide; and fourth, the condition of the kiln atmosphere.

"Clay free from iron oxide burns white. If a small quantity, say 1 percent, is present, a slightly yellowish tinge may be imparted to the burned material; but an increase in the iron contents to 2 or 3 percent often produces a buff product, while 4 or 5 percent of iron oxide in many cases makes the clay

¹ Clays, 81, 194 (1908).

burn red. There seems, however, to be not a few exceptions to the above statements. Thus we find that the white-burning clays carry from a few hundredths percent to over 1 percent of iron oxide, the more ferruginous containing more iron than the purer grades of buff-burning clays. Again, among buff-burning clays we find some with an iron oxide content of 4 or 5 percent, an amount equal to that contained in some red-burning ones. The facts, therefore, seem to indicate that the color of the burned clay is not influenced solely by the quantity of iron present.

"Seger has divided the buff-burning clays into two groups, namely: (1) those of such high iron contents as to burn red normally, but which are sufficiently calcareous to enable the lime to destroy the red iron color and form a yellow compound of iron and lime; and (2) those low in iron and high in alumina, which would normally burn pale red, but develop a yellow color due to the alumina-iron compound. He thus believes that the red coloration of the iron is destroyed by similar causes; but, on account of the lime being a stronger and more active base than the alumina, it is able to take care of a greater quantity of iron.

"Orton¹ has argued against the effect of alumina, claiming that, if this were true, synthetic mixtures should easily give the buff color, which, in his experience, it is not possible to produce. As he states, there is a great uniformity in the color of buff-burning clays, while their iron-alumina ratios fluctuate greatly; some fire-clays containing 40 percent of alumina and 0.5 percent iron, and yielding a good buff product, while others with 15 to 20 percent alumina and 2.5 percent iron burn to almost exactly the same tint. On the other hand, some clays with about the same alumina and iron content burn red. If Orton is correct, it would seem, therefore, as if the cause of this buff-burning quality must be sought for in some other direction.

"The evenness of color is apparently closely connected with the physical condition of the iron oxide, that in colloidal

¹ Trans. Am. Ceram. Soc., 5, 389 (1903).

form giving a uniformity of shade not obtainable by the admixture of very finely ground material.

"If a clay is heated at successively higher temperatures, it is found that, other things being equal, the color usually deepens as the temperature rises. Thus if a clay containing 4 percent of iron oxide is burned at a low temperature, it will be pale red, and harder firing will be necessary to develop a good brick-red, which will pass into the deep red and then reddish purple. Seger explained the successive shades of red by assuming that the iron oxide increased its density with rising temperature.

"The brilliancy of the color appears to be influenced by the texture, as the more sandy clays can be heated to a higher temperature, without destruction of the red color, than the more aluminous ones. Alkalies also appear to diminish the brightness of the iron coloration."

"Burned clays may be of many different colors. Although the majority of clays contain sufficient iron oxide to burn red, nevertheless it is not safe to predict, from the color of the raw clay, the shade that it will burn, since some bright red or yellow clays may yield a buff brick. If considerable iron oxide is present, 4 to 5 percent, the brick usually burns red, unless much lime or alumina is also present. An excess of lime in the clay will, however, counteract the effect of the iron oxide and yield a buff brick, but a brick owing its buff color to this cause will not stand as much fire as one which owes its buff color simply to a low percentage of iron oxide."

Burton¹ says: "The clays of earths from which burnt bricks are made may be divided into two principal types, according to chemical composition: (1) clays or shales containing only a small percentage of carbonate of lime and consisting chiefly of hydrated aluminum silicates (the true clay substance) with more or less sand, undecomposed grains of feldspar, and oxide or carbonate of iron; these colors usually burn to a buff, salmon or red color; (2) clays containing a considerable percentage of carbonate of lime in addition to

¹ *Encyclopaedia Britannica*, 4, 518 (1910).

the substances above mentioned. These latter clay deposits are known as marls,¹ and may contain as much as 40 percent of chalk. They burn to a sulphur-yellow color which is quite distinctive. . . .

"All clays contain more or less free silica in the form of sand, and usually a small percentage of undecomposed feldspar. The most important ingredient, after the clay-substance and the sand, is oxide of iron; for the color, and, to a less extent, the hardness and durability of the burnt brick depend on its presence. The amount of iron oxide in these clays varies from about 2 to 10 percent, and the color of the bricks varies accordingly from light buff to chocolate; although the color developed by a given percentage of oxide of iron is influenced also by the other substances present and also by the method of firing. A clay containing from 5 to 8 percent of oxide of iron will, under ordinary conditions of firing, produce a red brick; but if the clay contains 3 to 4 percent of alkalies, or if the brick is fired too hard, the color will be darker and more purple. The action of the alkalies and of increased temperature are probably closely related, for in either case the clay is brought nearer to its fusion point, and ferruginous clays generally become darker in color as they approach to fusion. Alumina acts in the opposite direction, an excess of this compound tending to make the color lighter and brighter. . .

"As before stated, the marls (which usually contain from 15 to 50 percent of calcium carbonate) burn to a yellow color which is quite distinctive, although in some cases, where the percentage of limestone is very high, over 40 percent, the color is gray or a very pale buff. The action of lime in bleaching the ferric oxide and producing a yellow instead of a red brick, has not been thoroughly investigated, but it seems probable that some compound is produced between the lime and the oxide of iron, or between these two oxides

¹The term "marl" has been wrongly applied to many fire-clays. It should be restricted to natural mixtures of clay and chalk such as those of the Paris and London basins.

and the free silica, entirely different from that produced by oxide of iron in the absence of lime."

Burton¹ repeats much the same facts without any explanation. "In ordinary clays, and with an oxidizing atmosphere, 1-2 percent of iron oxide produces a buff color, 2-4 percent a salmon color, and above 4 percent a red color, which becomes darker as the percentage of iron increases. The presence of other impurities, however, modifies the color produced by iron oxide considerably, and this is especially the case when a large percentage of lime or magnesia is present. Some clays (commonly called marls) contain from 15 to 30 percent of lime, and although they may also contain as much as 6-8 percent of iron oxide, they fire to a light yellow or buff color. Such clays are largely used for making the well-known yellow facing bricks, which were at first made chiefly from the marls of the Thames basin, the Paris basin, etc., and are now made from artificially prepared mixtures of clay and chalk or limestone."

Since there seemed to be no plausible explanation of the action of lime in causing bricks to burn yellow, Professor Bancroft suggested that I make a preliminary study of the problem as part of my senior research. The red color of bricks is admittedly due to the red ferric oxide or haematite. It is equally clear that the yellow color is due to an anhydrous yellow form analogous to limonite; but that does not get us ahead much because we do not know what limonite is or why lime should cause the formation of, or stabilize, an anhydrous limonite. It is customary among mineralogists² to classify the hydrates of ferric oxide as follows:

Haematite	Fe_2O_3	Limonite	$2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Turgite	$2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Xanthosiderite	$\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Goethite	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Limnrite	$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

Haematite occurs frequently in well-characterized crystals though often as an amorphous red mass or powder.

¹ Thorpe's Dictionary of Applied Chemistry, 2, 76 (1912).

² Robinson and McCaughey: Bureau of Soils, Bull. 79, 16 (1911).

Goethite occurs in nature as a definite crystallized hydrate; but van Bemmelen¹ has shown that a definite hydrate can be obtained in the laboratory only under special conditions, the decomposition of sodium ferrite by water at 15°. A definite hydrate is not obtained by the decomposition of potassium ferrite, for instance. No other hydrate of ferric oxide is known, so the formulas usually mean nothing more than that a hydrous iron oxide of varying water content happened to be analyzed under conditions such that the percentage composition could be represented approximately by the desired formula. Haematite is black when crystalline, though red by transmitted light, and its powder is red. Turgite is deep brown; limonite is a light brown or yellow,² while xanthosiderite,³ which is probably to be classed as limonite,⁴ is a golden yellow-brown to brownish red. Limonite is a full yellow.⁵ While it is generally true that the more hydrous the ferric oxide the yellower it is, this is not an absolute rule. Robinson and McCaughey⁶ say: "By heating limonite or any hydrate of ferric oxide, it loses water, changes color, and becomes, in fact, red haematite. There is, however, no satisfactory measurement of a temperature of inversion of limonite to haematite, and it is doubtful if such an inversion point exists. At ordinary pressures limonite does not lose water appreciably at any temperature which may be realized under field conditions.

"The literature on ferric hydrates is voluminous and contradictory. It appears, however, from laboratory investigations that ferric hydroxide, when first precipitated, is dark red. On standing it apparently becomes more compact,⁷

¹ Die Absorption, 145 (1910).

² A golden yellow oxide having the formula of limonite has been patented by Ramage and Sperry, U. S. Pat. 691,324 (1902).

³ Schmid: Pogg. Ann., **84**, 495 (1851).

⁴ Fischer: Zeit. anorg. Chem., **66**, 43 (1910).

⁵ Dammer's Handbuch der anorganischen Chemie, **3**, 304 (1893).

⁶ Bureau of Soils, Bull. **79**, 18 (1911).

⁷ [This statement must not be interpreted as meaning that the precipitate becomes coarser.]

and the color changes toward the characteristic yellow of limonite. Tommasi,¹ who has done much work on this subject, divides ferric hydrates into two series, *a* and *b*. The red or *a* series is obtained by precipitation with alkalis from solution. This series is easily soluble in dilute acids and is dehydrated by boiling. The yellow or *b* series is realized by the oxidation of ferrous hydroxide, ferrosoferric hydroxide, or ferrous carbonate. The *b* series is sparingly soluble in dilute acids and retains the water of hydration on boiling. The red or *a* series represents the condition of the freshly precipitated hydroxide. On standing it becomes yellow and occupies less bulk. Freezing and thawing and boiling hastens the process."

From this summary it is clear that the yellow color of certain hydrous ferric oxides depends on other factors than the percentage composition. With that settled for the moment we can now consider the effect of lime on the color of bricks. The yellow color cannot be due to calcium ferrite because Percy reports that this is black.² "I found that a mixture of sesquioxide of iron and lime in certain proportions yields a well-melted product. A mixture consisting of 160 grains of pure sesquioxide of iron and 100 of white marble (= 56 grains of lime)—that is in the ratio of Fe_2O_3 : CaO —was exposed in a covered clay crucible to a high temperature. It was perfectly melted, and when broken across resembled a black opaque, vitreous slag; the crucible had one large perforation. In a second experiment a mixture according to the same formula, of 40 grains of sesquioxide of iron and 25 of carbonate of lime, was heated in a clay crucible lined with platinum foil. It was perfectly melted and escaped through the crucible. Recently this reaction has again been investigated with the following results: An intimate mixture of 190 grains of sesquioxide of iron and 6.5 grains of lime was kept heated to whiteness in a platinum vessel during several

¹ Bull. Soc. chim. Paris, (2) 38, 152 (1882).

² Percy's Metallurgy: Fuel, 78 (1875).

hours in a muffle, the atmosphere of which is oxidizing, and left to cool in the furnace. The product appears to have been perfectly melted, and consisted of a mass of interlacing acicular crystals, exceeding an inch in length: lustre, dark bright metallic; fracture, uneven and lustrous; very brittle; when in powder resembled brown iron ore in color; sp. gr. 4.693; it was magnetic.

"Its percentage composition was found by analysis to be as follows:

Sesquioxide of iron	73.39
Protoxide of iron	0.72
Lime	24.50
Silica	1.35
Alumina	0.10
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	100.06

This compound may, in respect of composition, be regarded as *magnetite*, in which the protoxide of iron has been replaced by lime; or as a *spinel*, in which alumina has been replaced by sesquioxide of iron. It is analogous to the mineral termed *magnoferrite*, of which the formula is $\text{MgO} \cdot \text{Fe}_2\text{O}_3$."

I have tried heating various mixtures of rouge and lime and of rouge, lime, and alumina to different temperatures below those at which the mixtures fused. In no case was a yellow color obtained. This statement applies only to cases in which an appreciable amount of solid rouge is taken. It does not hold when an oxide is precipitated on or with the alumina.

The yellow color cannot be due to an iron silicate because ferrous silicate is a deep, olive-gray and ferric silicate appears to be instable.¹ "It is now known that when sesquioxide of iron is exposed to a high temperature, it is reduced to magnetic oxide without the intervention of any reducing agent; and that when a mixture of sesquioxide of iron and silica is strongly heated, even in the presence of atmospheric air, silicate of protoxide of iron is formed with evolution of oxygen."

¹ Percy's Metallurgy: Fuel, 71 (1875).

If the yellow color is not due to a calcium-iron or to an iron-silicate salt, the next hypothesis is the rather despairing one of Burton¹ that "some compound is produced between the lime and the oxide of iron or between these two oxides and the free silica, entirely different from that produced by oxide of iron in the absence of lime."

Percy reports upon a number of slags containing varying amounts of lime, iron oxide, alumina and silica.² No one of them showed any trace of yellow. Both red and yellow bricks fuse to slags like those recorded by Percy, thus showing that the hypothetical compound, if formed, must be stable at a lower temperature and, therefore, should be easy to isolate. If we were dealing with a definite compound of lime and iron, or lime, iron and silica, we ought to be able to get the color by heating a synthetic mixture of the ingredients. Orton³ has pointed out that other factors come in.

"The powerful influence of the physical factor is well realized by all who have tried to stain clays artificially to some particular tint. Iron oxide in masses of appreciable size becomes red on calcination at a low temperature, changing gradually to a bluish black as the temperature increases. When added to a clay, it appears as dark-colored grains in the matrix of the clay, which is itself changed little or none by this addition. Even when we grind ferric oxide to an impalpable powder, and distribute it into a clay most perfectly, it merely causes a darkening of the color, nothing like the buff or red colorations of natural clays.

"The failure of these simple synthetic attempts to produce iron colors in clays leads us to a study of the condition of the iron in natural clays. We find two states easily distinguished. First, the precipitated or colloid form, whose fineness exceeds all method of measurement and which we may fairly assume to be almost molecular. Second, the concretionary or granular form, in which its grains or crystals are of appreciable size.

¹ *Encyclopaedia Britannica*, 4, 519 (1910).

² *Percy's Metallurgy: Fuel*, 72 (1875).

³ *Trans. Am. Ceram. Soc.*, 5, 382 (1903).

"The precipitated form is necessary to the development of either a buff or red color. We may easily verify this by precipitating artificially some ferric hydroxide into a fluid slip of clay. It is possible to produce colors as uniform and as free from specks as natural clays but it is not possible to get some of the tints of natural clay or to get as much color for the amount of iron used as is developed by Nature's methods. As shown in discussing the origin of the shale clays, the iron has been associated with the clay minerals from the very time of formation. The primary clay was usually deeply stained by the solution of iron which formed with it. The soft gelatinous hydroxide has enveloped its grains from their very origin, and left each tiny particle covered by its coloring film. Every succeeding process tends to increase this uniformity, grinding, transportation, erosion, and deposition in swamps, all tend to increase the iron and to reduce its blend to perfection.

"Thus in the ordinary red-burning shale-clay, for instance, it becomes impossible to distinguish the hydroxide from the clay minerals. The sand, and the mica, and concretionary minerals of all sorts, can readily be separated by screens or by sedimentary processes, but the pulp which remains inseparable to the end, contains the bulk of the iron, and is red-burning, while the coarser matters which have been separated out, may burn light or dark or speckled, but hardly red. In fact, the question has been raised as to whether iron is not chemically combined as a part of the clay substance. No proof of this view has ever been attempted, and all the evidence obtainable points the other way."

Since there is no evidence of any binary or ternary compound of iron with lime and silica which is yellow, and since hydrous ferric oxide may be yellow, the most reasonable thing to do is to attempt to account for the yellow color in bricks as being due to ferric oxide in some way and not as being due to any compound with lime or silica. There is nothing impossible about this. In addition to ordinary silver we have blue, yellow and red silver, the color being a function

of the size of the particles. These forms of colloidal silver are not very stable as a rule; but this is largely a question of conditions. Baker¹ reports one case where colloidal silver was apparently stable enough to cause trouble in a technical process. Since this paper seems to have been overlooked by writers on colloid chemistry, I quote it in full.

"In some contributions to the metallurgy of lead, published in the *Philosophical Magazine* in 1862, I attributed a certain pink tint, occasionally seen in white-lead corruptions, to the presence of small quantities of copper. As the results of any experiments upon the corrosion of lead by the combined action of fermenting bark, acetic acid vapor, and atmospheric oxygen can only be arrived at after the expiration of ten weeks or three months, the progress of further investigation in this matter has necessarily been slow. I have been unable to isolate the coloring matter; but I wish to correct the statement that the pink color is due to copper, and to detail some conclusive proofs that it is caused by finely divided silver.

"Having obtained many tons of lead which contained only traces of copper, I found in several instances the pink color still quite evident in the corruptions. By the method which had been employed for refining the metal, there could be only silver left as an impurity in any perceptible amount. I, therefore, sought for evidence that this substance could produce such a result. Upon analyzing 5000 grains of a perfectly white corrosion, and of one which was distinctly and uniformly pink, the result showed that the two samples differed mainly in the amount of silver.

	CuO	FeO	NiO	Ag
White corrosion	0.0050	0.0022	trace	0.0005 ⁶⁶ / ₁₀₀
Pink corrosion	0.0060	0.0022	0.0013	0.0058 ⁶⁶ / ₁₀₀

"A small quantity of silver was then added to a portion of the lead which had produced the white corruptions, and this was again submitted to the corroding action. The result

¹ *Phil. Mag.*, [4] 37, 344 (1869).

was a decided pink carbonate. This synthetical experiment was repeated many times with a like result upon various samples of lead which had before produced a white carbonate; and I found that the pink color begins to show at the edge of the metallic portion left uncorroded when the silver amounts to more than 0.5 oz. per ton of lead. A decided color, which is uniform throughout the mass of the corrosion, is obtained when the silver amounts to about 1.5 oz. per ton. A fracture of a dense corrosion often shows the crystalline character of the metallic lead, which is defined to some extent by the pink color--as if the silver had segregated out at certain faces of the lead crystals. By the addition of a small quantity of arsenic or antimony the pink color was replaced by a dull purple; and a clear tint was only obtained when all the oxidizable metals had been removed.

"I come to the discussion of the state in which the silver exists to cause a pink or reddish reflection of light. Silver does not oxidize under the conditions of exposure to acetic acid vapor and oxygen of the air. Moreover oxide of silver and silver carbonate are themselves decomposed and reduced to a metallic state by a heat below that attained in the stacks of fermenting tan. The silver must consequently be in the metallic state. As confirming this statement I made the following experiments: Silver carbonate was triturated with white lead and water and then dried. Upon increasing the temperature, a delicate pink tint became visible upon the reduction of the oxide of silver. If a small quantity of silver carbonate be precipitated along with lead carbonate, the color upon drying and heating is more uniform, and it may be obtained exactly resembling the tint seen on white-lead corrosions.

"The color of the photographs obtained by means of silver salts is also evidence in favor of the metallic state of the silver, and I may also adduce the fact that a ray of light, when reflected ten times from a polished silver surface, is distinctly of a reddish color."

[According to Percy's Metallurgy: Fuel, 35 (1875), the color is golden yellow.]

We will start with the working hypothesis that the yellow color of ferric oxide is due to the very fine subdivision, in which case we should expect to get a yellow if we precipitated the hydrous oxide under conditions such that agglomeration would be kept down to a minimum, in other words in presence of another colloid. The production of a yellow by precipitating hydrous ferric oxide in presence of hydrous aluminum oxide appears to be used technically in the production of the so-called Mars pigments. Hurst¹ says: "Under the generic name of Mars colors the late George Field, a noted color manufacturer, introduced a series of yellows, oranges, reds, and violets, owing their color to ferric oxide. Field did not publish any account of the method by which he produced these colors; but descriptions of similar products have been given by various French and German writers on pigments. These colors present no advantage over ochres and iron-reds as regards permanency or brightness of tone, but have disadvantages as regards cost. Mars yellow is made by taking equal weights of ferrous sulphate and alum, and adding a solution of carbonate of soda, thereby precipitating the iron and alumina; the precipitate is collected, washed well with water, and dried slowly. Mars orange is made by slightly calcining the yellow; Mars red is made by calcining the yellow at a red heat; Mars violet is made by calcining the yellow at a white heat. By using milk of lime instead of the soda salt the colors could be made cheaper, a plan which is in use in making some forms of iron-reds. Mars brown was made in a similar manner from a mixture of ferrous sulphate, alum, and manganese chloride. Mars colors can be distinguished from the ochres and ochre-reds by being soluble in strong hydrochloric acid, and by containing a large proportion of alumina but no silica."

Church² says that Mars yellow "is a kind of yellow ochre prepared artificially. It may be made by precipitating a salt of iron mixed with alum by means of caustic soda, or

¹ *Painters' Colors, Oils and Varnishes*, 151 (1901).

² "The Chemistry of Paints and Painting," 157 (1901).

potash, or lime. The salts of iron used are either green vitriol (ferrous sulphate) or the ferric chloride. If green vitriol be employed, the precipitate gradually becomes yellow on exposure to the air. Upon the proportion of alum mixed with the iron salt depends the depth of the yellow color in the product, for the alumina precipitated with the iron hydrate acts as a diluent of the color. When lime is used as a precipitant for the iron compound (if this be green vitriol or ferric sulphate), calcium sulphate, that is, gypsum, comes down also with the ferric hydrate and basic ferric sulphate, and serves to lighten the color.

"By submitting the different varieties of Mars yellow to various degrees of heat, with or without a little nitre, a number of products of different hues are obtained, including Mars orange, Mars brown, and Mars violet. All these preparations require very thorough washing to fit them for use on the palette of the artist.

"The Mars colors are permanent when carefully prepared and thoroughly purified from soluble salts. They seem sometimes to have a slightly injurious effect upon a few of the best semi-permanent pigments of organic origin, such as the madder colors. This action may be due to the ferric hydrate in them combining with the coloring matter, and displacing some of the alumina previously united with it. In this direction it is probable that Mars yellow will be more active than the deeper-colored pigments produced by calcining it at various temperatures."

Bersch¹ recognizes the possibility of obtaining the color without using alumina. "Mars yellow, which is generally reckoned among the best artists' colors, is usually a mixture of ferric oxide and calcium sulphate or alumina. The pigment is prepared by mixing a solution of ferrous sulphate with milk of lime, when ferrous oxide is precipitated, which becomes yellowish brown on exposure to air, in consequence of the oxidation of the ferrous oxide. By heating the precipitate,

¹ "Manufacture of Mineral and Lake Pigments," 155 (1901).

according to the temperature, different shades are obtained varying between yellow and red. In addition to Mars yellow, Mars orange and Mars red are found in commerce.

"The manufacture of this pigment is very simple: 1 part of ferrous sulphate is dissolved in 10 parts of water, and the solution mixed with milk of lime made from 1 part of quicklime and 40 parts of water. If it is desired to produce a darker shade, and especially a product to be afterwards converted into Mars orange, the amount of ferrous sulphate is increased to 2 parts. When the mixture had been made, it must be stirred for a long time, in order that the reacting substances may come thoroughly into contact. The precipitate, which at first is greenish gray, soon acquires by the action of the air the color of ferric hydroxide, which becomes deeper on drying.

"When dried and finely ground Mars yellow is heated in thin layers, it changes to dark yellow, and finally to orange-red, a similar alteration taking place to that occurring when ferric hydroxide itself is heated.

"A Mars yellow of a deeper shade, consisting of a mixture of ferric hydroxide and alumina, is obtained by precipitating with caustic soda a solution of ferrous sulphate and alum. The sodium sulphate, which is formed at the same time, must be removed as completely as possible by washing with boiling water.

"By calcining Mars yellow for a long time at a high temperature, Mars brown is produced, a fine brown pigment. The value of Mars yellow and the pigments obtained from it lies not only in their fine shade, but in their permanence, which distinguishes the majority of the iron colors."

Toch¹ mentions the Mars colors but gives no information in regard to the way they are made and ignores the alumina content. In regard to Mars orange he says that "this has sometimes been called extract of burnt sienna, because it is composed entirely of hydrate oxide of iron which has been properly precipitated and washed. It is very uniform in

¹ "Materials for Permanent Paintings," 140 (1911).

composition, and identical with ordinary iron rust. It has generally been regarded as a perfectly safe and permanent pigment, but this is not a fact. It attacks not only every lake with which it may be mixed, but is such a hard drier that it has a tendency to crack. It makes most beautiful clear yellowish tints when mixed with zinc white, and when diluted with constant white, it has every characteristic of a lake; but, owing to its chemical composition, it darkens upon extreme exposure, and the beautiful clear tones which it produces when mixed with white have a tendency to sadden upon exposure.

"Mars red is similar in all respects to Mars orange with the exception that it has been heated until the water of combination is driven off, and while it is identical with light red, it is much more transparent. It is a soft, permanent color, and although it is supposed to affect a number of lakes, it is very doubtful whether it does; but, in order to practice precaution, it may be wise not to mix it with several of the lakes but to use the lakes over it as a glazing color. It dries well and is permanent.

"Mars violet is a very dark form of crocus martis, or Indian red. It is similar to the color known as caput mortuum, and is nothing more or less than a purple oxide of iron. It has a distinctly bluish shade, is very durable, dries well and is permanent to light.

"Mars yellow has also been called extract of ochre, or extract of raw sienna, because it is composed of the coloring matter of these two pigments. It frequently cannot be distinguished from a good quality of raw sienna, is permanent, dries well, and is translucent. It has been suggested frequently that Mars yellow, or a good form of raw sienna, should be used as a substitute for the yellow lakes; and this can easily be done when these colors are mixed with constant white. As a glazing color it is permanent; but, like all of the oxides of iron which contain water in combination, it must not be mixed with an organic color such as one of the lakes."

Nobody seems to have bothered himself with the ques-

tion why a yellow is possible under these circumstances. The existence of yellow ochre in nature has convinced the painter that hydrous iron oxide does occur in a yellow form and he has naturally let it go at that. From the published accounts it is quite clear that we are dealing with an irreversible reaction, the yellow hydrous oxide agglomerating on heating to an orange, brown or red form on heating, the change being also accompanied by a loss of water. It is not a question, strictly speaking, of Tommasi's two series because it is possible to obtain a yellow either by oxidizing hydrous ferrous oxide or by precipitating hydrous ferric oxide, whereas Tommasi's theory called for a yellow color in the first case and a red one in the second. On the assumption that the yellow form is the one with the finest particles, it is easy to see that the simultaneous precipitation of hydrous alumina would tend to make the color yellow. It is not exactly obvious why one should get the same result when lime water is added to a ferrous sulphate solution containing no aluminum sulphate. The only explanation to be offered for this at present is that the simultaneous precipitation of calcium sulphate prevents the agglomeration of the yellow pigments to the red pigment.

In order to have some first-hand knowledge in regard to the Mars colors a few qualitative experiments were made. Two parts of ferrous sulphate and two of aluminum sulphate were dissolved in forty parts of water. To this was added a solution of one part of lime in eighty of water. A dirty green precipitate was formed which gradually oxidized and became yellowish brown. When air-dried the color was a light ochre. When heated slightly it darkened somewhat, the color becoming a raw sienna. Increasing the amount of ferrous sulphate in the first solution gave a darker shade while increasing the amount of lime gave a lighter shade. One part of ferrous sulphate plus three parts aluminum sulphate plus caustic soda gave a bright yellow precipitate. When washed and air-dried the color was a yellow ochre. When heated this sample darkened considerably, while further heating changed it to an iron oxide red.

In another run the aluminum sulphate was omitted. One part of ferrous sulphate was dissolved in ten parts of water. To this was added one part of lime dissolved in forty of water. The precipitate was green at first and then oxidized to a brownish yellow which was a shade darker than in the preceding runs. On heating, this behaved quite differently from the others, changing to an olive-gray.

When a fairly concentrated solution of ferric chloride was boiled, a bright yellow precipitate was obtained which turned the characteristic red on heating, the one heated to the higher temperature being more of a purple-red.

Instead of using lime or caustic soda as a precipitating agent, we may use sodium carbonate. Equal parts of ferrous sulphate and aluminum sulphate in the dry state were mixed thoroughly and then a solution of sodium carbonate added. This gave a yellow ochre verging on the orange. Increasing the amount of ferrous sulphate darkened the color. Increasing the amount of aluminum sulphate seemed only to make the color lighter. When heated these went over into a reddish brown, changing at the highest temperatures (in the blast lamp) to a brownish black. A good deal more work on these colors had been planned; but the loss of time due to the fire in Morse Hall cut down the time available. The experiments show the same general results as those given in the books. One would like, of course, to know why the presence of lime and the absence of alumina caused the precipitate to turn an olive-gray when heated. It looks as though this would not be difficult to work out but it would need time. One thing is clear, however, and that is that the alumina tends to keep the iron oxide from turning red, which is exactly what should happen if the yellow color is due to the iron oxide being in a very finely divided state. The analogy between the Mars colors and the yellow bricks is not a close one because the yellow in the pigments is due to hydrous iron oxide while this is undoubtedly not the case with the bricks. The Mars colors are cited as being technical products in which the fine division of the iron oxide is maintained by alumina.

According to the theory as outlined, the alumina seems to be the prime factor in determining the yellow color of bricks. With clay high in alumina we get yellow or buff bricks for a suitable percentage of iron. If we keep the iron constant and reduce the percentage of alumina, we get a clay which burns red. If we add lime to our clay, the lime will combine with the silica when the clay is heated, setting free alumina and the brick will burn yellow or buff. It is therefore the free alumina which counts and not the total alumina. The general conclusion may, therefore, be formulated that a clay containing three to four percent of iron oxide will burn red if the free alumina is low and yellow or buff if the free alumina is high. The question of how to determine the amount of free alumina can fortunately be left to somebody else. This explanation can be checked very simply. If the importance of lime consists in its setting free alumina, the addition of an acid like sulphuric acid should cause the appearance of the red color, quite regardless of whether we assume that calcium sulphate and aluminum silicate are formed or calcium silicate and aluminum sulphate. This has actually been observed by Biedermann and Gabriel.¹ There had been trouble owing to the formation of red patches on yellow tiles. Analysis showed that the red spots contained considerably more sulphate than the yellow portions, the sulphate being present apparently as calcium sulphate. The trouble was, therefore, due to sulphuric acid in the kiln gases.

Since the alumina in the Mars colors does not prevent the agglomeration of the ferric oxide, when it dehydrates, it was hoped that perhaps a yellow brick would turn red if heated to a higher temperature. Unfortunately the brick tends to vitrify before it turns red. The experiment was an interesting one because it brought out several points which had not been foreseen by us though perfectly familiar to ceramists as we learned later. A piece of a commercial yellow brick was heated in an electric furnace. Although

¹ Ber. deutsch. chem. Ges., **10**, 1548 (1877); Kerl: Handbuch der gesammten Thonwarenindustrie, 512 (1907).

the brick was exposed to the air, an apparent reduction took place and the resulting slag was of a dark green color. The brick was next heated in an oxyacetylene flame, but again reduction took place. Much better results were obtained on using a blast lamp. The brick assumed a decidedly red shade which was most marked at the surface. It is not surprising that the effect is less striking than with the Mars pigments because these latter contain a great deal more iron. When Mars yellow was mixed with a large excess of BaSO_4 , SiO_2 , etc., and heated, it turned red much less rapidly. The apparent reduction of the iron oxide is really a dissociation into a lower oxide. At high temperatures ferric oxide breaks down into ferrous oxide and oxygen.¹ When the brick vitrifies, ferrous silicate is formed. If the brick cools in an oxidizing atmosphere, the ferrous silicate breaks down to ferric oxide and silica. It is, therefore, not surprising that the red color should be more marked at the outside. This matter of re-oxidation has been discussed by Hull.² "When a dark or 'flashed' burn is finished, top, middle and bottom trials are all nearly black and their predominant color is green or bluish green. If the brick could be taken out of the kiln at that stage and chilled quickly, as is done with the trials, the brick would be as dark as these finishing trials. In practice the reverse is true. The cooling, in ordinary practice, takes place under more or less strongly oxidizing conditions. The tendency is for oxidation to take place rapidly while the brick are still at high temperature and at a gradually lessening ratio during the progress of the cooling, down almost to atmospheric temperature. This reoxidation, following the reduction, brings the color back through various combinations towards the red, and the result is a kiln of brick of a variety of colors in all of which red, yellow, blue and green are intimately intermingled in various proportions. The colors of the finished product are dependent to so great an extent upon the chemical

¹ Percy's Metallurgy: Fuel, 50, 71 (1875); Orton: Trans. Am. Ceram. Soc., 5, 425, 429 (1903); Kinnison: *Ibid.*, 16, 136 (1914).

² Trans. Am. Ceram. Soc., 16, 185 (1914).

changes which take place during the cooling, that this process lays special claim to the burner's study. The problems of the control of reoxidation are fully as important as those of the reduction period. If there were no reoxidation, strongly reduced kilns would turn out, as is indicated above, nearly black bricks in which the colors would be a combination of green and blue, with the green predominating."

It is now possible to discuss the very careful and interesting work of Binns and Makely.¹ They started with an English plastic ball clay to which they added iron in different forms and various mixtures of ground quartz and pure alumina. The resulting masses were burned at 1200° C and at 1270° C. They recognize that adding quartz and alumina in this particular way is not quite fair. Of course, the adsorption is quite different from what it would be with hydrous alumina. Even under these unfavorable conditions the alumina tends to change the color to buff, the effect being most marked the higher the alumina content, the higher the temperature and the lower the iron content. They themselves say that alumina is undoubtedly responsible for the production of buff colors and in this the opinion of Seger is confirmed. In one series the iron was added "as commercial ferric oxide, the whole mixture being ground together in water in a porcelain ball mill. An inspection of the results shows that no red color can be expected from this source. The prevailing tone is a pinkish gray, the color being somewhat lightened as the content of alumina increases. At the lower fire the alumina produces no change in hue but simply a lighter tint. This is probably due to the fact that the alumina is more bulky than the quartz and consequently the whitening effect is greater. At the greater heat, however, the tone of the color is changed, as the alumina increases to buffs of varying strength. This is especially the case at the 5 percent iron content though it is apparent in every instance. . . . It is not possible to produce red colors in burned clay by the use of pulverized iron-bearing minerals, however finely they may be ground;

¹ Eighth Int. Cong. Applied Chem. New York, 5, 7 (1912).

but buff tones are produced under the influence of alumina and at a temperature at which the clay approached vitrification. These buff colors are apparently due to the blending of a multitude of minute brown specks."

It is not surprising that iron oxide powder does not color the bricks red. To produce a maximum color the iron would have to be distributed as nearly uniformly as possible over the grains constituting the body of the brick. This is obtained to a certain extent by addition of ferrous sulphate solution and subsequent precipitation of the hydrous oxide. Binns and Makely say that "red colors are the result of the precipitation of a colloidal iron compound in the clay mass." This precipitation apparently results from a solution of ferrous sulphate, which is itself the result of the oxidation of pyrite, either becoming oxidized with the separation of limonite or meeting with carbon dioxide in some form with the resulting precipitation of ferrous carbonate. This is the only way of explaining the statement of Prof. Orton, quoted above, that "as good a red color may be developed from a clay containing its iron as ferrous carbonate as from ferric hydroxide." Siderite does not decompose under ordinary conditions and in the finely ground form no red is produced.

"Pyrite is responsible for several phenomena. As already stated it is the parent of other forms of iron, and, while it is true as stated by Orton that the granules of pyrite 'are never small enough to produce a red color,' it is also true that pyrite is extremely susceptible of oxidation. Unless the clay containing this mineral is dried very rapidly, ferrous sulphate and ultimately ferric hydroxide will be found. There are examples of this in the specimens shown; in fact, in these there is the actual birth of a red clay."

At the high temperatures the alumina evidently peptized the iron oxide in spite of the former being present in granular form.

While the analogy of the yellow bricks with Mars yellow is striking and helpful, it has been pointed out that the iron oxide in the Mars colors is hydrated, while this is probably

not the case in a yellow brick. In fact a yellow-burning clay becomes red before it turns yellow.¹ It is, therefore, necessary to consider whether an anhydrous yellow iron oxide is possible. No such substance seems to have been produced in a pure state. Tommasi² claims that the anhydrous oxide of the "red" series is brown and that of the "yellow" series is red or reddish yellow. The yellow oxide might easily be stabilized by other substances and, as a matter of fact, we find that iron may produce a yellow color in glass,³ where there can certainly be no water. "It is generally admitted that oxide of iron gives a greenish color to glass to the mixture of which it has been added; but the truth is, that this color is produced *only* in peculiar circumstances. The manufacturers of china, porcelain and earthenware, are well aware that oxide of iron is the coloring material of a fine *purplish red* enamel fired in their muffle (and it is quite clear that *enamels* are real *glass*); if the temperature were raised too high, this enamel would lose its purplish tinge and tend towards *orange*; so that three colors of the spectrum are produced by oxide of iron, even at the degrees of heat which I should call *low*, compared with the temperature of furnaces for glass melting, which we shall now consider.

"If into a pot containing white melted glass or flint glass we introduce during the blowing a small fragment of iron, it will, from its gravity, fall to the bottom; now, if after the blowing this pot is taken out of the furnace, we shall see close to the fragment of iron partly oxidized, a portion of the glass colored from *orange* to *yellow*. We have also an illustration of the *yellow* color produced by oxide of iron in the manufacture of artificial *aventurine*. It is known that this *aventurine* is produced by the exposure of soft glass containing a large proportion of the oxides of copper and iron, to a temperature below its fusion: during this exposure the

¹ Orton: Trans. Am. Ceram. Soc., **5**, 402 (1903).

² Bull. Soc. chim. Paris., (2) **38**, 152 (1882).

³ Bontemps: Phil. Mag., (3) **35**, 440 (1849); cf. Shaw: Trans. Am. Ceram. Soc., **16**, 142 (1914).

copper is produced in the form of metallic crystals, and the glass being colored only by the oxide of iron, takes a *brownish yellow* color; and the greater the reduction of the copper the yellower is the glass."

Mène¹ writes formulas for the iron colors: Fe_2O_3 gives purplish red; $\text{FeO} \cdot 3\text{Fe}_2\text{O}_3$ gives orange-red; $2\text{FeO} \cdot \text{Fe}_2\text{O}_3$ gives yellow; $\text{FeO}_3 \cdot \text{Fe}_2\text{O}_3$ gives green; $3\text{FeO} \cdot 2\text{Fe}_2\text{O}_3$ gives blue and $6\text{FeO} \cdot \text{Fe}_2\text{O}_3$ black; but there is no proof for any of this.

If the theory as outlined here is correct, it should be possible to obtain a buff product which would stand heating by precipitating a relatively small amount of ferrous hydroxide along a relatively large amount of alumina. This experiment has been carried out successfully by Mr. Scheetz in the Cornell laboratory. It is, therefore, evident that an anhydrous yellow ferric oxide can be obtained provided agglomeration is prevented. While alumina is probably the most important agent in preventing the iron in bricks from changing from yellow to red, it is not claimed for a moment that other factors may not come in. Thorp² says that quicklime, when pure, is white and amorphous; but iron gives it a yellow tint. In this case we evidently have anhydrous ferric oxide in a finely divided state. Desch³ states that Roman cements have a dark brown color, owing to the presence of considerable quantities of ferric oxide.

Orton⁴ has brought out an interesting point in regard to carbonaceous matter. "It seems as if some other influence than the amount of iron, its distribution, or its masking by other oxide must be brought in to explain the buff-burning fire-clays. The significant fact is that fire-clays occur so very generally in connection with coal veins or other accumulations of organic matter; wherever carbon has been accumulated in bygone ages, there we find buff-burning clay imme-

¹ Kerl: *Handbuch der gesamten Thonwaarenindustrie*, 513 (1907).

² "Outlines of Industrial Chemistry," 177 (1916).

³ "The Chemistry and Testing of Cement," 41 (1911); cf. Köhl and Knothe: "Die Chemie der hydraulischen Bindemittel," 67 (1915).

⁴ *Trans. Am. Ceram. Soc.*, 5, 389 (1903).

diately underneath. Often the coal has been washed away while still soft, and disseminated; but the fact that it had been there is proven by the fire-clay vein which is left behind. In fact, the fire-clay more uniformly marks the coal swamp than the coal itself.

"This connection, so constantly shown, all over the world, in strata of all ages where coal has grown, certainly seems significant. Whether the swamp growth has formed certain organic salts of iron which influence the color, or whether it is by the removal of other substances than iron, or whether it is by stimulating the growth of concretionary forms of iron and thus preventing the distribution of the color, cannot be stated.

"On the other hand, in support of Seger's theory that alumina masks the iron and produces the buff color, the fire-clay beds of New Jersey, the flint clays of Missouri, and many of the Cretaceous fire-clays of Germany, may be cited. They do not occur in connection with coal veins, nor is it reasonable to suppose that they are composed by the erosion of other carboniferous fire-clay beds, and deposited without sensible blending or intermixture with red burning sediments. In fact, their occurrence, alternating with beds of sand, gravel, and red clays, gives the lie to any such assumption.

"The most we can say at present on the cause of buff color of the fire-clay groups, is that they generally contain less iron than is needed to produce a red color; that this iron is distributed in the most perfect manner possible. Seger's alumina theory does not seem to wholly fit the case, and the geological history of fire-clays and their production by swamp growth and carbon accumulation is after all not a cause. There must be a difference in compound, or amount, or distribution, or their geological history could hardly avail to produce a difference. The settlement of this most interesting point is one which invites the attention of the ceramic investigator."

The matter seems rather simple as stated. In presence of decaying organic matter, the iron oxide will come down in an extremely finely divided form and may easily retain enough

adsorbed organic matter to cut down very greatly the agglomeration of the iron oxide on heating. The whole argument of this paper is that the yellow color caused by iron is due to sufficiently finely divided ferric oxide. The medium plays no part directly though it may play a very important one indirectly because some media will be much more effective than others in preventing agglomeration.

While it does not come properly within the scope of this paper, there is one interesting point to which reference may be made. Red bricks are apt to turn pink or even buff when heated¹ to a temperature just short of vitrification. This is undoubtedly connected with the dissociation of ferric oxide, but the details seem to be somewhat uncertain. Michaelis² believes that an olive-green calcium ferrite is first formed and that the green and the pink are complementary colors forming white. Kinnison gives no very clear explanation; but he seems to favor the view that ferric oxide breaks down to ferrous oxide which then reacts to form ferrous silicate. A peptizing action by the alumina may also be a factor. In any case it is quite clear that a great deal more work needs to be done on the colors of colloidal ferrous and ferric oxides.

Some experiments were made on grinding the red oxide of iron with water and with gelatine solution in the hope of obtaining a yellow oxide; but the experiments were unsuccessful and had to be given up when the laboratory burned. It is planned to repeat them at some future time under more favorable circumstances.

The general conclusions to be drawn from this preliminary paper are:

1. The yellow color of bricks is due to iron oxide and not to a compound of iron oxide with lime or silica or both.
2. The yellow color is due to ferric oxide in a very finely divided form; when the particles are larger the color is red.
3. Alumina seems to be the important peptizing agent in the bricks and the color is yellow when the ratio of free alumina to iron is high.

¹ Kinnison: *Trans. Am. Ceram. Soc.*, **16**, 136 (1914).

² Kerl: *Handbuch der gesammten Thonwaarenindustrie*, 513 (1907).

4. The effect of lime is chiefly an indirect one in setting free alumina.

5. In Mars yellow the color is due to a hydrous iron oxide; but this can hardly be the case in bricks and cannot be the case in glass.

6. The dyeing of cotton an iron buff or khaki is apparently analogous to the formation of Mars yellow.

7. While no anhydrous yellow ferric oxide has ever been prepared pure, it may be and evidently is stabilized by other substances.

8. When a small percentage of ferrous hydroxide is precipitated along with a large percentage of aluminum hydroxide, the buff color of the heated product is undoubtedly due to anhydrous ferric oxide.

9. The yellow color of slightly impure quicklime is due to anhydrous ferric oxide.

10. When clay is deposited in presence of organic matter, the iron oxide is likely to be precipitated in a very finely divided state. Such clays may burn buff without the lime or the alumina content necessarily being high.

11. There is enough alumina in the Mars pigments to prevent the formation of a red color until the iron oxide becomes anhydrous; but not enough to keep the anhydrous ferric oxide yellow. With less iron oxide a buff color is obtained which will stand heating. It is probable, though not proved, that such a color would be more stable than the usual type.

12. In so far as agglomeration is more marked at high temperatures, yellow bricks should turn red if heated hot enough. On the other hand, the peptizing action of the alumina increases with rising temperature. With bricks this latter seems to be the predominating factor, because red bricks become paler or even buff when heated.

13. The changes of color, when yellow bricks are heated, are complicated by the dissociation of the ferric oxide. Heating in oxygen should be tried.

14. A great deal more work must be done before we can account satisfactorily for all the colors produced by iron in soils, pottery and glass.