Permanent Color Standards for Fats, Oils, and Other Colored Liquids

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Introduction

Owing to the increasingly wide use of colorimetric methods of analysis and material grading, the matter of preparing permanent color standards is coming to be one of considerable importance. The oil, soap, varnish, petroleum, brewing and tanning industries in particular make use of color standards for the specification of raw materials and finished products, and for process control in the course of manufacture. The work to be described in the present report was undertaken for the purpose of preparing a set of color standards duplicating the colors of the well-known FAC standards developed by the A. O. C. S. and A. C. S., but of improved permanency. Although the object of the investigation was a specific one, much of the information obtained was of a general character and will, it is believed, be of interest to anyone who has occasion to prepare or use color standards for one purpose or another.

Requirements of a Color Standard

The requirements of the ideal color standard which is to be used for all-round purposes, be it colored glass, dyed gelatine, or a solution of either organic or inorganic nature, are very definite and, it may be added, very exacting. First of all, and most obviously, it must match accurately the substance it is intended to represent. Second, it must be capable of precise duplication. Third, it must be obtainable at a minimum of expense. Fourth, it must be easily manipulated in actual practice. Fifth, it must not undergo change of any kind in use. None of the types of standards that have yet been proposed fulfill all these requirements perfectly. In choosing a standard to meet a particular need, it is usually necessary to sacrifice one or more of the less important requirements in favor of others which are considered more essential.

Taken as a class, the glass standards do not give exact matches, are difficult to duplicate, are fragile, expensive and usually have to be used with a rather costly instrument of some kind. They do, as far as we know, possess the advantage of permanency. Dyed gelatine has many of the disadvantages of glass without the advantage of permanency. Solutions of organic substances, particularly dyestuffs, provide an unlimited variety of colors but are difficult to standardiže and unstable in the light. Inorganic salt solutions, although somewhat restricted in range of color, seem to have most of the other qualifications demanded of a color standard. They are readily standardized and therefore capable of exact duplication.

Although expense, or rarity, prohibits the use of some members of this class which might otherwise be desirable, several are easily obtained at low cost. Certain inorganic salts are very permanent when exposed to light. Temporary changes in color due to variations in temperature do, however, sometimes take place. Another disadvantage of commercial inorganic salts is that they all contain small amounts of impurities which are precipitated in time, especially if the solutions be very concentrated. It is nevertheless possible, with care, to prepare solutions of inorganic salts of very good permanency, which are well adapted to use as colorimetric standards.

It will be interesting to consider the FAC standards, with which the present work is principally concerned, to see to what extent they fulfill the requirements of a color

standard. As far as actual color is concerned, they have been found to cover in a satisfactory manner the ordinary range of color of commercial oils and fats. Some little trouble has been experienced in the exact duplication of sets, due to variations in the size of the tubes and possibly to changes in the solutions themselves. The difficulty with the tubes is not, of course, peculiar to the FAC standards, but would be experienced with solutions of any kind. The expense of preparation is within reason. They are very convenient to use; may be easily carried about, and a determination of color is made in a few moments with a minimum of skill and effort. In this respect they have a decided advantage over such instruments as the Lovibond Tintometer, and other tintometers and colorimeters, although the latter have been found very satisfactory for laboratory measurements. In only one respect does it seem desirable to improve upon the FAC solutions; that is in their resistance to the effects of light.

Exposure tests on the FAC standards have revealed that, although the darker colors are stable enough for all ordinary purposes, certain of the light tints are so fugitive as to render the probability of their undergoing change in average use one of considerable importance. When exposed to the ordinary diffused light of the laboratory, numbers 1, 3 and 5 were somewhat faded in less than a week. Tubes No. 7 to 11A and 13 to 19 were faded in three weeks. The fading in some instances was pronounced. 1, 3 and 5, for example, were completely decolorized in three weeks or less. Numbers 11B, 11C, and 21 to 45 were unchanged after a month in diffused light.

The action of direct sunlight is, as would be expected, much more rapid. 1 and 3 are decolorized in a day, and 5 to 11A, 13 and 15 are decolorized in a week. All of the light colors, that is, tubes 1 to 19, are badly faded in a week. 21 to 45 were unchanged after two weeks in the sun, but all were faded, some of them badly, in a month or less. It is, therefore, evident that some improvement in permanency, particularly among the very light colors, is desirable. The work that will be described herein was undertaken with this object in view.

Substances Heretofore Used as Color Standards

A search of the literature revealed a considerable number of materials recommended for use as color standards in work of widely divergent nature. Platinic potassium chloride and cobalt chloride solutions, suggested by Hazen in 1892¹, have been used for many years as standards in water analysis. Cobalt chloride and cupric chloride were recommended for nitrite determinations by Jackson in 1900². Kendall and Richards 1904³ used potassium chromate as a standard in nitrogen determination, and mixtures of potassium dichromate and cobalt sulphate for ammonia. Washburn⁴ used mixtures of ferric chloride, cobalt nitrate, and copper sulphate in a colorimetric method of estimating arsenious acid.

Arny^{5, 6} has for a number of years recommended mixtures of cobalt chloride, ferric chloride, and copper sulphate in 1 per cent hydrochloric acid as standards for general colorimetric work. These standards, which are called the "Co-Fe-Cu" fluids, have been advocated specifically for cottonseed oil color work⁷. They are said to be stable for many years. Other workers^{8, 9} have recommended Arny's solutions. For obtaining colors not available with the Co-Fe-Cu combination, Arny suggested solutions of roseo-cobaltic chloride, ammonium dichromate, and copper sulphate in 2.8 per cent ammonia water. These standards unfortunately precipitate after a few months. For certain pinks, reds, and violets Arny proposed potassium bichromate and permanganate, but such mixtures are unstable and have to be used within an hour or two after they are prepared.

For measuring the color of varnishes, Wertz¹⁰ suggested a fresh solution of potassium bichromate in sulphuric acid. A 3 per cent solution of this reagent is used at the present time as a standard for interior varnish by the U. S. government¹¹. Fonrobert¹² recommended iodine-potassium iodide solutions for a similar purpose, expressing the color number as the number of milligrams of free iodine in 100 c.c. of solution. Gardner and Holdt¹⁸ advocated caramel dissolved in water with one-half per cent of sodium benzoate added to prevent bacterial action. These solutions were not faded after six weeks' exposure to the ordinary light of the laboratory. Atkinson and James¹⁴ adopted solutions of nickel sulphate and iodine-potassium iodide mixed in various proportions to match the colors of varnishes.

Other workers have used various combinations of the salts already mentioned to prepare standards for pH determinations. The experience of many observers seems to point to the conclusion that the colored inorganic salts are more suitable than other substances for use as permanent color standards. The only published tests that give any idea of the comparative stability to be expected of the different colored salts are found in the work of Mellon and Foster¹⁵, who reported that certain salts of copper, cobalt, nickel, and iron, dissolved in water acidified with hydrochloric acid, are unchanged after one year's exposure to sunlight. Nowhere in the literature was any disadvantage attending the use of such solutions mentioned.

A survey of the literature leaves several important questions unanswered. First, just how do the inorganic salts compare with dyestuffs and other organic coloring matters in stability? Many authors have said that the former are superior, but quantitative information is lacking. Second, what are the disadvantages of the inorganic salts? Third, what is the relation between concentration and stability? One would expect that very dilute solutions would lose color more quickly than concentrated ones. The matter of preparing stable light-colored solutions is of particular interest. Fourth, are there any other colored salts available besides the ones mentioned in the literature? And fifth, the immediate object of the present investigation, what are the best salts to use for preparing a set of solutions of good permanency, duplicating the FAC colors? In the work to be described, answers were sought for the foregoing questions.

Exposure Tests on Various Substances in Glycerol

In the present set of FAC standards, glycerol is used as the solvent in order to give them the appearance of viscous oils. In our initial tests, attempts were made to find suitable coloring matters which would prove stable in the same medium when exposed to light for a considerable length of time.

The method followed in determining fastness to light was to prepare solutions of the various substances approximately equal in color intensity to FAC standard No. 3, place them in thick-walled glass test tubes of 10-11 mm. inside diameter, fitted with cork stoppers for organic liquids and rubber for inorganic, and expose them in an upright position on the roof where they received the direct rays of the sun all day long. Duplicate solutions were kept in the dark.

Eighty-six dyestuffs were tested in glycerol in this manner. The great majority of them were badly faded after one day's exposure. Only three were unchanged after two-weeks' exposure: Rhodamine B, Quinoline Yellow, and Primuline. Rhodamine B was faded in a month, Primuline in two. Quinoline Yellow proved to be very stable and was not changed by six months' exposure to sunlight. Both yellows were suitable only for matching the lighter colors, however, and the Rhodamine B could not be used on account of its pronounced fluorescence.

The tests on dyestuffs in glycerol, therefore, failed to provide the necessary range of permanent colors for the purpose in view, and further, gave evidence that dyestuffs as a rule are unstable when dissolved in glycerol, at least at very low concentrations. Whether or not a more extended search would yield a sufficient variety of stable colors it is impossible to say. This line of attack was abandoned in favor of more promising methods.

Ferric chloride, cobalt chloride, nickel chloride, iodine and potassium dichromate were next tried in glycerol, and all except the cobalt and nickel salts faded within a week. No stable inorganic yellow salt could be found, and the use of inorganic coloring matters in glycerol was thereby precluded.

Solutions of caramel of various concentrations in glycerol, giving colors ranging from FAC No. 1 to 45 were the third type of coloring matter tested. A set of ten standards of this nature have been used for oils and fats by us for many years, and have been found satisfactory. The three lightest colors of the set, equivalent to FAC Nos. 1 to 7, were very slightly faded in a week, and the remaining ones were unchanged. After two weeks, the next four darker ones, including colors up to FAC No. 19 were only slightly faded. This type of standard is therefore faster to light than the present FAC's. The only drawback is that this set does not cover as wide a range of colors as the FAC set, so that extremely yellow oils and those of a greenish cast cannot be matched with it.

The tests on various substances in glycerol clearly indicated that the number of coloring matters stable in this solvent is very limited. Subsequent tests were therefore conducted largely on aqueous solutions, on the assumption that the property of viscous appearance is of secondary importance to that of permanency.

Exposure Tests on Dyestuffs Dissolved in Water

One hundred and nine water solutions of dyestuffs were tested for fastness to light, following the procedure previously described. Of these, the following thirteen were not faded after three weeks' exposure (May, 1933) to direct sunlight.

Tartrazine Solantine Yellow FF Conc. Pheno Fast Yellow 3 AP Metanil Yellow MXX Conc. Fast Wool Yellow 3 GL Fastusol Yellow RTD Extra Fast Yellow No. 104 Tropaeolin G Direct Fast Yellow BD Conc. Acid Orange A Fastusol Green BL Xylene Blue Patent Blue AN

There appears to be little or no relation between the fastness of a dyestuff in solution and on the fibre, although several of the colors listed above are known to possess good fastness on the fibre. It is evident that dyestuffs in general are more stable to light in water than in glycerol. Reds, it will be noticed, are lacking in the above list. The best reds found were Fast Red A and Pontamine Scarlet 4 BS, which were unchanged by one week's exposure. Distilled water, boiled just before using, was employed in all of these tests; but in spite of these precautions fuzzy agglomerates were sometimes found, especially in the tubes kept in the dark, due perhaps to the growth of micro-organisms of some kind present in the water. This is another thing that must be looked out for in using dyestuffs as color standards. The only dyestuffs which withstood the sun test for two months were Pheno Fast Yellow 3 AP and Fastusol Yellow RTD.

When mixtures of the foregoing comparatively stable dyestuffs were tried out, it was found that they were not so stable as the individual colors tested alone. Furthermore, in one case, at least, there was a departure from the rule that more concentrated solutions are more stable than dilute ones. For instance, mixtures of Fastusol Yellow RTD and Fastusol Green BL, of color intensity equal to FAC No. 3, were not faded in a week; but the same two colors, when mixed to match the darker FAC tubes, 21-25, and 31-35, faded badly in a week. Satisfactory matches of FAC tubes 27, 29 and 37-45 were obtained with Acid Orange A and Fastusol Green BL and although these solutions withstood the action of sunlight for five weeks, still their permanency was not all that tests on the individual colors would have indicated.

These tests were sufficient to show that the extreme permanency desired could not readily be obtained with dyestuff solutions. There seems to be no doubt, however, that certain dyestuffs in water may serve as color standards of moderate fastness to light, although the fact that an individual color is stable alone does not mean that it will prove stable when mixed with other dyestuffs. For the immediate purpose of the present investigation, inorganic salts were found to be so much more permanent that our attentions were largely directed along this line of effort.

Before describing the tests on inorganic salts we will record briefly some experiments made on certain colored organic substances of natural and synthetic origin which showed that this class of material is unstable and of restricted color range.

Tests on Natural and Synthetic Colored Substances

The following substances were exposed to direct sunlight and all found to fade in two weeks or less:

		•
Substance		Faded In
Crude glycerine	.Water or C.P. glycerine	2 weeks
	.None	
Palm oil	.None	2 weeks
Dark tailow	.None	2 weeks
p-nitroaniline	.Dilute H Cl	2 weeks
Oil of Vetiver	Benzene	2 weeks
Oil of Patchouli	Benzene	2 weeks
Caramel	.Water or normal H Cl	1 week
Dynamite glycerine	.None	1 week
Crude glycerine	.N. H Cl or N. NaOH	1 week
Cresylic acid	.C.P. glycerine	1 week
	.Benzene	
	.Benzene	
Wheat germ oil	.Benzene	1 week
Light Tallow	.Benzene or none	1 week :
Dark Tallow	.Benzene	1 week
Olive oil	.Benzene	. 1 week
a-nitronaphthalene	.Benzene or glycerine	1 week
Linseed oil	Benzene	. 1 week
	. Benzene	
Oil of cloves	.Benzene	. 1 week
	.Benzene	
Oil of thyme	.Benzene	. 1 week
Oil of cassia	.Benzene	. 1 week
	.Benzene	
	.Benzene	
Thymol	.Benzene	1 week
	.Benzene	
Amylene dichlorides	.Benzene	1 week
Oleic acid	.Benzene	. 1 week
Paraffin base cylinder oil.	. Benzene	. 1 week
	. None	
Yellow corn dextrine	.Water	1 week
Pyridine	.Glycerol	. 1 week
Turkey Red Oil	. Carbon tetrachloride	, 1 week

From the foregoing tests it is evident that the colors present in most natural oils and many synthetic compounds are not at all stable in the light. The action of light is not always one of bleaching; paraffin oils and quinoline become darker.

Tests on Inorganic Substances

The colored substances available among inorganic compounds have been classified by Mellon¹⁶. The transi-

		(Color in Soluti	ion)		
Element	Acetate	Chloride	Sulphate	Nitrate	Bromide
Chromium (ic)		Two forms, Violet and Green	Violet and Green	Violet and Green	
Iron (ic)	Brownish Yellow (dil. sol.) Brownish Red (conc.)	Yellow (dil.) Brownish Yellow (conc.)	Yellow (dil.) Brownish Yellow (conc.)	Colorless (Yellow in conc. HNO ₃)	Yellow (dil.) Brownish Red (conc.)
Cobalt (ous)	Red in glacial or dil. acetic acid	Water: Red (dil.) Violet (conc.) HCl: Violet (6n) Blue (8-12n)	Red	Red	Red (water) Violet (48% H Br)
Nickel (ous)	Green in water or acetic acid	Green (water) Greenish Yellow (8 n H Cl) Yellow (conc. H Cl)	Green	Green	Green (water) Olive Green (48% H Br)
Copper (ic)	glacial acetic acid	Blue (dil.) Green (conc.) Yellow Green in 8 n H Cl	Blue	Blue	Green
Uranium (yl)	Yellow	Yellow	Yellow	Yellow	

Table I. Colored Salts of Common Metals (Color in Solution)

tion elements of the periodic system (Fe, Co, Ni and their homologues) and certain of the neighboring elements, such as copper and chromium, have color-forming properties. In addition, the elements Bromine and Iodine are colored, as are certain complex anions such as Cr_2O_7 , MnO_4 , $Fe(CN)_6$ and Pt Cl₆. The rare earths, also form colored compounds. Many of the known colored inorganic substances are too rare to be used as color standards.

In the following table is given a list of the common colored inorganic salts, together with some notes on their colors in solution.

The more common of the colored anions, and their colors in solution are listed below:

Anion	Color in Solution
Chloroplatinate	
Chromate	
Gobaltinitrite	
Dichromate	. Yellow (dil.), orange (conc.)
Ferricyanide	.Yellow
Nitroprusside	.Brownish yellow (dil), red (conc.)
Permanganate	.Bluish red (dil.), purple (conc.)
Polysulphide	.Yellow

In Table II is given a list of the inorganic solutions on which exposure tests were made. The exposures were carried out in the manner previously described, all solutions being of a concentration sufficient to produce a color of intensity approximately equal to that of FAC No. 3. The solvent used was distilled water, except where stated otherwise.

Table II. Stability of Various Colored Inorganic Solutions

(In concentrations giving a color intensity equivalent to FAC Std. No. 3)

1110 510. 110. 0)	
	Effect of Exposure to
Solution	Direct Sunlight
Ferric chloride—n. HCl	Unchanged in 4 months
Uranyl chloride	Unchanged in 4 months
Cobalt chloride	Unchanged in 4 months
Cobalt sulphate	Unchanged in 4 months
Cupric chloride	.Unchanged in 4 months
Cupric sulphate	Unchanged in 4 months
Sodium chromate	Unchanged in 4 months
Colling distances	Unchanged in 3 months
Sodium dichromate	Unchanged in 3 months Faded in 4 months
	Unchanged in 1 month
	Faded in 5 weeks
	Unchanged in 2 months
Nickel sulphate	Faded in 3 months
Nickel chloride	Unchanged in 2 months
	Faded in 3 months
Potassium chromate	Unchanged in 3 weeks
	Faded in 4 weeks
Chromic fluoride	Unchanged in 3 weeks
	Faded in 4 weeks
Vanadium ovytrichloride	Unchanged in 2 weeks
Vanadium oxytrichloride	Faded in 3 weeks
Platinic potassium chloride	Faded in 1 wk or less
Sodium chromate n. HUL	. Faded in 1 wk. or less
Potassium dichromate n. HCl	Faded in 1 wk or less
Ferric ammonium sulphate n. HCl	Faded in 1 wk. or less
Ferric oxalate	.Faded in 1 wk. or less
Ferric thiocyanate	.Faded in 1 wk. or less
Ferric chloride (neutral solution)	Faded in 1 wk. or less
Bromine water	.Faded in 1 wk. or less
Iodine-potassium iodide	.Faded in 1 wk. or less
Sodium nitroprusside (neutral)	.Faded in 1 wk. or less
Soduim nitroprusside (n. NaOH)	.Faded in 1 wk. or less
Sodium nitronrusside (n. HCl)	Faded in 1 wk or less
Sodium cobaltinitrite (n. NaOH)	.Faded in 1 wk. or less
Sodium cobaltinitrite (neutral)	.Faded in 1 wk. or less
Sodium cobaltinitrite (n. HCl)	.Faded in 1 wk. or less
Sodium thiocarbonate (n. NaOH)	.Faded in 1 wk. or less
Sodium thiocarbonate (n. NaOH) Sodium ethyl xanthate (n. NaOH)	. Faded in 1 wk. or less
Sodium polysulphide (n. NaOH)	. Faded in 1 wk. or less
Potassium permanganate (neutral) Potassium permanganate (n. H_2SO_4)	Faded in 1 wk. or less
Potassium permanganate (n. H ₂ SO ₄)	. Faded in 1 wk. or less
Potassium permanganate (n. KOH)	. Faded in 1 wk. or less

It should be noted that the results tabulated above do not check the work of Mellon and Foster, in certain cases. The latter investigators reported the following substances stable for a year in the sunlight.

K ₂ Cr O ₄	HC1
$K_2Cr_2O_7$	—HCl
Iodine	— KI
Iodine	-glycerol

We found these substances faded after a week's exposure. The cause of the difference possibly lies in the concentrations of the solutions used and the conditions of exposure. We purposely employed very dilute solutions, because such solutions are known to fade more quickly than ones of higher concentration. In our tests the samples were placed outdoors where they received direct sunlight all day long, while in the tests of Mellon and Foster, the samples were exposed indoors in such a way as to receive the direct sunlight available through a southern window.

The most stable common inorganic salts are, therefore, ferric chloride acidified with HCl, uranyl chloride, cobalt, copper, and nickel salts, sodium dichromate and chromate. All of these, except uranyl chloride, sodium chromate and sodium dichromate have been used as color standards in work published by previous investigators. An advantage possessed by sodium dichromate over potassium dichromate is its much greater solubility which permits of a wider range of colors. Also, it is faster to light, at least in the concentration tested. With the foregoing salts it is possible to obtain a great many shades of red, orange, brown, yellow, green, blue and violet. All except sodium chromate may be used together in solution. Hydrochloric acid should not be used in solutions containing dichromate as it lowers the permanency.

Duplicating the FAC Standards with $FeCl_3$, $CoCl_2$, and $NiCl_2$ in n. HCl

It was found possible to duplicate all of the FAC colors using combinations of FeCl_3 , CoCl_2 , and NiCl_2 in normal hydrochloric acid. A set of color tubes using these salts was therefore prepared and exposed to light. These standards were found to be exceptionally permanent; none of the solutions faded in six months, but Nos. 1 and 3 showed signs of slight fading after seven months in the sun. As far as permanency is concerned, therefore, these solutions leave little to be desired.

An unforeseen difficulty appeared in the fact that these standards were very sensitive to temperature changes; a difference of five degrees C. in some cases was sufficient to produce a pronounced change in color. This property is illustrated in the following table (Table III), which gives the appearance of each tube at 31° C. compared with a duplicate tube kept at 21° C.

Similar tests on the original FAC standards showed no change in color on heating 10 or 20 degrees C.

Tests on the individual salts revealed that the one chiefly responsible for the changes in color was ferric chloride, which becomes deeper in color when warmed as little as five degrees. Cobalt chloride and nickel chloride change when heated 25° C. or more, but the color change for ordinary variations in room temperature is negligible. It is thus evident that any color standards making use

Table III. Effect of Temperature Variation on the Color of FeCl₃ Stds.

The Marcal and	Change in Color
Tube Number	When Warmed 10° C.
1	
3	
5	Slightly yellower
7	Slightly yellower
9	Slightly yellower
11,	Darker
11A	Darker
11B	Darker
11C	
13	
15	
17	
19	
21	
23	
25	
27	
29	
31	
33	
35	
37	
39	
41	
43	
45	Very much darker!

of ferric chloride must be used always at a definitely specified temperature. This detracts considerably from the ease of making a color determination, although it might possibly be argued that the increased permanency would more than compensate for the loss in convenience. Efforts were made to modify the standards so that the element of temperature could be disregarded.

A number of salts of iron and other metals in solutions of various acid concentrations were tried out in an attempt to find one which would exhibit no color change. It was discovered that ferric chloride in 8 n. H Cl may be heated 40° C. or more without changing the color, but unfortunately, cobalt chloride is blue in this solvent and no red salt is available. Ferric acetate showed practically no color change on heating, but its color is lacking in yellow and furthermore, the acetates are not sufficiently soluble to give all of the dark shades.

As a result of further tests it was found that although all inorganic salts change color if heated sufficiently, yellows are available in the form of sodium dichromate and uranyl chloride which change less than ferric chloride. Accordingly, sets were prepared using these yellow salts, in conjunction with salts of cobalt and copper.

Another characteristic of the ferric chloride standards is one that has been found common to all the commercial inorganic salts; that is, the property of depositing precipitates on prolonged standing. An examination in October, 1933, of sets prepared in August, 1932, revealed a small precipitate in tube No. 45, and a smaller one in tube No. 29. No precipitate of appreciable size was found in any of the other tubes, but small precipitates could be seen in bottles containing 250 c.c. of the darker solutions, Nos. 21-45.

All of the inorganic salts examined in the present work have been found to deposit more or less of solid matter from concentrated solution, on prolonged standing. Dilute solutions give less precipitate or none at all. The precipitates are larger when certain salts are mixed; for example, on mixing copper sulphate and sodium dichromate. It is thus evident that preliminary treatment of the reagents is necessary if the color standards are to be free from all imperfections.

Standards Containing Sodium Dichromate, Cobalt Sulphate, and Copper Sulphate or Chloride

All of the FAC solutions may be duplicated with combinations of these salts in distilled water. Copper sulphate is used for all colors except 27, 29, 43 and 45, in which cupric chloride is employed. Exposure tests made on standards of this type have shown that the lighter colors (1-19) will resist the action of sunlight for one month, while the darker ones (21-45) do not change color in six months' exposure. They are therefore superior to any dyestuff combinations yet found, as far as permanency is concerned.

Changes in temperature have some slight effect on the color of these standards, but the extent of the change is such that no difficulty should be found in ordinary conditions of use.

The matter of precipitation has been found somewhat troublesome in mixtures containing sodium dichromate. This difficulty was not experienced with the light colors (1-19), but the darker ones (21-45) deposited a yellowish precipitate, which on analysis, was found to contain lead, chromium, and a trace of iron, and probably consists chiefly of lead chromate. An attempt was made to overcome this by adding sulphuric acid, making the concentration .1 normal, but the method was not wholly efficacious and the permanency of the standards was impaired, although they were still capable of withstanding two weeks' sunlight without change. Purification of the reagents was also tried, but even after three crystallizations a little precipitate was obtained on mixing.

This difficulty was finally overcome by letting mixtures of sodium dichromate with each of the other salts stand in concentrated solution until all or nearly all of the precipitate had been thrown down. This treatment requires at least a month. After filtering, the mixtures are used in place of the separate solutions for preparing the standard colors. Solutions made up in this manner gave no precipitates on two months' standing, either in tubes or in the 250 c.c. stock bottles.

In addition to the precipitate referred to in the foregoing, certain of the very dark solutions were found to have a few dark particles in them after they had stood for a long time. These particles differed in appearance from the granular lead chromate precipitate, and analysis of them showed copper and a trace of iron present. Their formation was accelerated by exposure to light, or by heating. This difficulty was overcome by adding a small amount of acid. Nitric acid had less effect on the permanency of light than sulphuric, and a concentration as low as .01 normal was sufficient to prevent the deposition of solid matter on heating. In the solutions finally adopted a concentration of .02 normal HNO3 was used.

It is believed that the matter of precipitation in inorganic color standards can, in some cases, be overcome by simply aging until the traces of the less soluble impurities have come down. A somewhat more rapid method suggested is to let concentrated solutions of the reagents stand before using, filtering from time to time to find out when precipitation has ceased. Preliminary heating seems to hasten the reaction. When a constituent of one reagent, as, for example, the trace of lead in copper sulphate, is likely to react with another reagent, such as sodium dichromate, it is necessary to allow mixtures of the salts to stand. The method is not as rapid as could be desired, but it seems to be the only simple way of getting rid of substances likely to precipitate.

Standards Containing Uranyl Chloride, Cobalt Chloride, and Cupric Chloride

It is possible to match standards 1-19, excepting 11C, with mixtures of these three salts. Standards of

this kind proved to be more stable to light than the corresponding colors made with sodium dichromate. No change occurred in four months' exposure to direct sunlight. (May-August, 1933.)

Like most inorganic solutions, they change color slightly as the temperature varies, but the color change is less than in the case of ferric chloride and the only precaution necessary is to avoid extreme changes of temperature. Where absolute color accuracy is desired, a definite temperature may be specified.

The first set of standards prepared with uranyl chloride gave no precipitates, but the second set made with uranyl salt from a different source showed a precipitate in tube 11B and a smaller one in No. 19, and traces in some of the other tubes. The precipitate, on analysis, turned out to be silica. It is therefore advisable to treat the reagents in the manner previously recommended, in order to remove the less soluble impurities.

The New Proposed Set of Color Standards for Fats and Oils

As a result of the work that has been described, it is proposed to adopt a new set of solutions, for which greater permanency is claimed, in place of the present solutions of dyestuffs in glycerol which compose the present set of PAC color standards. The following solutions are recommended:

- 1 to 19 inclusive (except 11C)-uranyl chloride, cobalt chloride, and cupric chloride in distilled water.
- 11C, 21 to 25, and 31 to 41 inclusive-sodium dichromate, cobalt sulphate and cupric sulphate in .02 normal nitric acid.
- 27, 29, 43 and 45-sodium dichromate, cobalt sulphate and cupric chloride in .02 normal nitric acid.

It is recommended that the solutions be kept in sealed tubes of soft glass, inside diameter 10.3 mm. \pm .3, outside diameter 12.8 mm. \pm .3.

Color standards prepared according to our formula have been tested for permanency in the Fadeometer, a form of carbon arc lamp widely used in testing dyed fabrics for fastness to light. No fading occurred in any of the colors in 119 hours. FAC standards 11B, 17, 31, and 45 were tested simultaneously and all faded in 23 hours. Another set was exposed to direct sunlight outdoors and did not fade in two months. These tests are being continued. The lightest FAC tube now in use, it will be recalled, fades in a day, and the darkest in a month.

The new standards, therefore, represent a considerable improvement in regard to permanency.

As has been stated, some variation in color occurs when the temperature changes. In the following table (Table V) the color at 34° is compared with that at 22° C. Warming the standards 12° produces a slight change in some of the dark ones, but it is in no case equivalent to the color difference existing between two successive standards.

Table IV. Effect of Temperature Change on the **Proposed Standards**

Std. No.	Color at 34° C.
F.A.C. Scale	(Compared with duplicates at 22° C.)
1	
3	
5	
9	Very slightly yellower
11	
	Very slightly darker
11B	
11C	
13	Same

15 17	
19	Same
21	
23	
25	
27	Slightly darker
29	
31	
33	
35	
37	. Slightly darker
39	
41	Voru alightly darker
43	Slightly darker
7 J	. Sugnuy ualker

From the foregoing observations it is evident that extremes of temperature have to be avoided when color readings are made with the proposed standards. If the solutions are made to match perfectly at 25° C., they may be used anywhere between 20° and 30° without serious error.

Color Standards for General Purposes

Using the inorganic salts recommended in the present report, color standards may be prepared covering a wide range of colors and for a variety of purposes. The colors available in permanent form are the following:

 $Red-CoSO_4$ or $CoCl_2$

$$Orange = Na_2 Cr_2 O_7$$

- Yellow—FeCl₃ in HCl, UO₂Cl₂, and Na₂Cr₂O₇

Green—CuCl₂, NiSO₄, and NiĆl₂ Blue—CuSO₄, CoCl₂ in 8n. HCl. Violet—CoCl₂ in 6n. HCl

Solutions of these salts are more stable in the light than any class of material that has yet been proposed for color standards, except glass. The stability generally increases with the concentration of salt. As has been pointed out, solutions of this nature possess certain disadvantages which have to be considered in selecting materials for a particular standard. Chief of these are the variations in color that occur when the temperature changes, and the formation on long standing of small precipitates in the solutions, due to impurities. If these factors are given proper consideration in the preparation of the solutions, it is quite practicable to prepare color standards of superior permanency, possessing no undesirable features.

Summary

1. The requirements of a satisfactory all-round color standard are stated.

2. The advantages and disadvantages of the present FAC oil and fat color standards are considered.

3. Systems used as colorimetric standards by previous workers are summarized.

4. Tests are described which show that glycerol solutions of dyestuffs are usually fugitive to light, and that comparatively few other coloring matters are stable in glycerol.

5. Tests are described which show that solutions of dyestuffs in water are more stable than in glycerol, but do not possess the extreme permanency desired of a color standard.

6. Further tests are outlined which indicate that the colors of other organic substances, of natural and synthetic origin are generally unstable when exposed to light.

7. The common colored inorganic salts are listed.

8. Tests showing the extreme permanency of certain inorganic salt solutions are described. The most stable ones are: Fe Cl₃— H Cl, UO₂ Cl₂, Co Cl₂, Co SO₄, Cu Cl₂, Cu So₄, Na₂Cr₂O₇, Na₂Cr O₄, Ni Cl₂, and Ni SO₄.

9. The disadvantages of inorganic salts are discussed.

These are (1) variations of color with temperature and (2) the formation of precipitates on standing. A method of overcoming the latter is given.

10. Color standards of three kinds, duplicating the FAC colors are discussed.

11. A new and more permanent set of solutions is proposed to displace the solutions of dyestuffs in glycerol, used in the present FAC fat color standards.

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- **Sulphonated Oil Committee Appointments**

CUPPLEMENTING the announcement in the February issue of OIL AND SOAP Dr. Eugene R. Manning of Clemson College in North Carolina, has been appointed a member of the

New Committee on Methods of Analysis and

Grading of Sulphonated Oils, with Particular

Reference to the A. A. T. C. C. Modifications.

Following is the complete committee, which is now functioning under the leadership of Ralph Hart of New York:

- Ralph Hart, Chairman, 1440 Broadway, New York City.
- J. Andrew Clark, Dutchess Bleachery, Inc., Wappinger Falls, N. Y.
- Prof. A. H. Grimshaw, North Carolina State College, Raleigh, N. C.
- W. H. Irwin, Swift & Co., Chicago, Ill.
- M. F. Lauro, New York Produce Exchange, New York City.
- C. P. Long, The Procter & Gamble Co., Ivorydale, O.
- H. H. Mosher, care Onyx Oil & Chemical Co., Jersey City, N. J.
- R. A. Pingree, The U. S. Finishing Co., Providence, R. I.
- M. L. Sheely, Armour Soap Works, Chicago, Ill.
- W. H. Tiffany, U. S. Testing Co., Inc., 1415 Park Ave., Hoboken, N. J.
- Ralph Wechsler, National Oil Products Co., Harrison, N. J.
- Dr. Eugene R. Manning, Clemson College, Clemson, North Carolina.

Complimentary Dinner for New Chairman

The following members of the American Oil Chemists' Society were present at an informal dinner at the Chemists' Club in New York City on Wednesday evenining, February 14th.

W. A. Peterson, Ralph Hart, J. Andrew Clark, W. H. Tiffany, M. F. Lauro,



Ralph Hart, Chairman

T. A. Marshall,

E. T. Marceau,

David Wesson,

J. Wrench,

- C. V. Serbell,
- J. P. Harris,
- E. A. Sigworth,
- H. H. Mosher.

This dinner was complimentary to Ralph Hart, chairman of the new committee on the study of sulphonated oils and the other new members of the Society.