When gasoline only is to be treated, the filtering operation may, of course, be dispensed with. The foregoing is an outline of the process as carried out on the distillate from Persian oil. The purification is so effective that with gasoline from Persian oil, containing originally the percentage of sulfur indicated above, the regular commercial output passed the following tests:

1—100 cc. gasoline + 1 cc. KMnO_4 (0.1 N soln.) + 2 cc. 10 per cent sulfuric acid, and vigorously shaken retains the permanganate color for 10 min., usually much longer.

2—When a sample of the gasoline is treated with sodium and alcohol and, after the reaction is over, slightly acidified and tested with lead acetate, no film of lead sulfide can be detected.

3—The copper dish test is entirely negative.

4—The Doctor test is negative.

The Composition of Erythrosin¹

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ALTHOUGH tetraiodofluorescein was discovered in 1875, the commercial purification of its sodium salt was not well understood even in 1909, as is evidenced by the statement of E. G. Kohnstamm² before the Seventh International Congress of Applied Chemistry in that year: "Of twelve samples of erythrosin examined, ten were not erythrosin at all, and of the other two, one was low in iodine, and one contained arsenic." To-day, with the dyestuff standing as one of the seven permitted food colors and receiving important consideration as a sensitizer of photographic plates, the subject of its preparation has attained considerable importance. When intended for use as a food color, it is obviously necessary to place the requirements in regard to purity as near the theoretical as technical practice will allow. The failure, however, of carefully made and apparently pure technical erythrosin to conform to the standards set by the United States Bureau of Chemistry³ has made it seem doubtful if the formula $\text{C}_{20}\text{H}_6\text{O}_4\text{I}_4\text{Na}_2$, as given in Schultz's *Farbstofftabeln* for 1914, page 200, and as adopted by the Bureau of Chemistry, is correct.

In this communication are submitted the results of a study concerning: (a) the preparation and purification of tetraiodofluorescein, (b) the conversion of this into the sodium salt—i. e., erythrosin, (c) the composition of pure erythrosin, and (d) the composition of the technical product.

PREPARATION OF TETRAIODOFLUORESCIN

Fluorescein was prepared in the usual manner from phthalic anhydride, resorcinol, and zinc chloride, and was carefully purified. Its purity was further confirmed by converting a portion into the diacetate, and this was found to melt at 199° to 200° C.⁴

Three methods are described in the literature for the preparation of tetraiodofluorescein: (1) the electrolysis of an alkaline solution of fluorescein containing a little excess of iodine;⁵ (2) the treatment of a comparatively cool alkaline solution of fluorescein and sodium iodide with ammonium or potassium persulfate;⁶ and (3) direct halogenation in hot dilute acetic acid with an excess of iodine.⁷ For laboratory preparation this last method seemed to offer the best possibilities.

Twenty-four grams of fluorescein were dissolved in a hot mixture of 24 cc. of 30 per cent sodium hydroxide and 240 cc. water. One hundred grams of iodine and 240 cc. of water were treated with just sufficient 30 per cent sodium hydroxide solution (105 cc.) to cause decolorization, and the two solutions were mixed and heated nearly to boiling. One hundred grams of glacial acetic acid were allowed to flow in drop by drop, with good stirring, the temperature being maintained at nearly the boiling point. The liquid was then partially neutralized with 55 cc. of the sodium hydroxide solution, and, after short standing, made strongly acid with 200 cc. of 1:1 hydrochloric acid. After boiling for a minute, the mixture was diluted with hot water to 3 liters, and the whole allowed to stand for several hours. The yield of crude, amorphous product was 95 per cent.

It was found that the method of Mühlhauser—namely, repeated digestion with dilute hydrochloric acid—did not remove all the adhering iodine. Treatment of an alkaline solution of the dye with sodium sulfite apparently removed some of the halogen even from the molecule itself. Repeated digestion with sodium iodide gave a product very light in color, but which still retained some iodine, as could be demonstrated by heating the acid at 135° C., whereupon vapors of iodine were given off. Treatment with 5 per cent sodium thiosulfate solution was not efficient, and there always resulted a slight precipitate of sulfur. The following procedure was finally adopted for securing a product which, while amorphous, was free from occluded and adsorbed iodine: four washings of the crude substance with water containing a little sulfuric acid in order to repress the solubility of the iodo compound, two extractions with warm alcohol, then solution in dilute sodium hydroxide (50 g. dye in 3 l. of water), and precipitation, hot, with dilute sulfuric acid; then again washing with water, and finally with alcohol. The final product was very light in color and did not give off iodine vapors when heated for one hour at 150° C.

The product thus purified, while entirely free from occluded iodine, contained about 6 per cent of diiodofluorescein, as was evidenced by its iodine content—59.74 instead of 60.75 per cent. It is almost impossible to separate completely the tetraiodo from the diiodo compound by recrystallization of the mixture of the acids, because the two are nearly alike in respect to solubility, or rather insolubility, in the usual solvents. Nor can one depend upon the melting point as a criterion of purity, for this is very indefinite. In order to obtain perfectly pure tetraiodofluorescein, we have therefore converted our product into the diacetate, purified the latter by recrystallization until the melting point was constant and iodine analysis indicated a compound of unques-

¹ Received May 8, 1922.

² *Proc. 7th Internat. Cong. Appl. Chem.*, 1909, Sec. 4b, p. 122.

³ "Coal-Tar Colors Used in Food Products," U. S. Dept. Agr., Bull. 147, 206.

⁴ Baeyer, *Ann.*, 183 (1876), 2, 13.

⁵ *Chem. Zentr.*, 1900, II, 1176. Société chimique des Usines du Rhone, Anct. Gilliard, P. Monnet, et Cartier; D. R. P. 108,838.

⁶ Winther, "Patente der Organischen Chemie," 2 (1877-1905), 169.

⁷ Mühlhauser, *Dinglers polytech. J.*, 263 (1886), 99; 263 (1892), 258.

tioned purity. This diacetate upon saponification gave us the pure tetraiodofluorescein.

TETRAIODOFLOURESCIN DIACETATE—25 g. of tetraiodofluorescein, 100 cc. of acetic anhydride, and 5 g. of fused sodium acetate were heated in an oil bath under a reflux condenser for 2 hrs. at 150° C., and the solution was then poured while still hot into ice water. The solidified mass, washed with water and dilute sodium hydroxide, and dried, was recrystallized from boiling bromobenzene. It then became soluble in cold acetone, from which, however, it almost immediately reprecipitated as a beautifully crystalline white powder, nearly insoluble in all solvents of low boiling point. By three crystallizations from bromobenzene, alternated with the above-mentioned solution and precipitation from acetone, a pure white product was obtained which melted at 293° to 294° C. Yield, 14 g.

Calculated for diacetate $C_{24}H_{12}O_7I_4$: I, 55.20 per cent.

Found: I, 55.27; 55.46; 55.08; 54.90. Av. 55.18 per cent.

SAPONIFICATION OF THE DIACETATE—Of several methods tried, the following was found most suitable: 10 g. of erythrosin diacetate were suspended in a mixture of 600 cc. of acetone, 45 cc. of water, and 90 cc. of ammonium hydroxide solution at room temperature for 8 to 10 hrs., complete solution having been effected in about one-third of this time. The filtered solution was diluted with one-fourth its volume of water and, after partial neutralization with dilute acid, heated to 40° to 50° C. Upon complete acidification, pure acid precipitated crystalline. In this condition the air-dried material retains only 0.5 per cent of solvent. Yield, 95 per cent. The acid purified through the diacetate could readily be obtained in crystalline form even from its warm aqueous ammoniacal solution by dilute acetic acid, complete separation being insured by finally adding a little sulfuric acid. The same material precipitated in the cold was amorphous, but when sufficiently washed was equally pure.

Per cent				
Calculated for $C_{24}H_{12}O_7I_4$: I,		60.75		
Found: Lot 1 I,	60.44	60.51	60.67	Av. 60.54
Lot 2 I,		60.62		
Lot 3 Hot pptn. I,	60.43	60.27	60.73	Av. 60.54
Cold pptn. I,	60.65	60.56	60.65	60.81 Av. 60.67

Tetraiodofluorescein thus prepared is insoluble in all the usual solvents which boil below 100° C., with the exception of alcohol and moist acetone, and only slightly soluble in these. Ethylene chlorobromide and dibromide dissolve a little on heating, as does bromobenzene, but the precipitates obtained on cooling are not fully crystalline. The solubility in ethyl salicylate is low. Nitrobenzene dissolves 1 g. per 15 cc. at 160° C., but at best only half of this is precipitated on long standing, and the product is somewhat low in iodine content. *m*-Cresol proved an unusually good solvent at its boiling point, but here again the yields were never better than 50 per cent and the product analyzed only 59.37 per cent iodine.

METHOD OF IODINE ANALYSIS—For the determination of the percentage of iodine, the Pringsheim method, fusion with sodium peroxide, proved entirely unsuitable. The chromic acid oxidation according to Baubigny and Chavaunne⁸ was applicable and has been used to some extent, but the results were inferior in constancy to those obtained by the method of Seeker and Mathewson,⁹ as is shown on the same sample in both cases, in the following table:

Per cent Iodine	
Baubigny and Chavaunne	50.09; 47.89. 48.29; 48.99
Seeker and Mathewson	48.90; 48.99; 48.94

Some slight modification of the second method, however, was found advisable, especially in the case of acid dried

for a long time. 0.2 to 0.3 g. of tetraiodofluorescein was dissolved in 20 cc. of water and 10 cc. of 10 per cent sodium hydroxide by heating gently for a few minutes. (With the sodium salt, only 2 cc. of sodium hydroxide are necessary.) While still hot, 40 to 60 cc. of a saturated solution of halogen-free potassium permanganate were added, followed by 12 to 15 cc. of concentrated nitric acid. The subsequent treatment was identical with that given by Seeker and Mathewson. It was found that this method of halogen estimation could be applied to the diacetate also, if the sample were dissolved in 30 cc. of 70 per cent alcohol and 15 cc. of 10 per cent hydroxide, and heated on the water bath until all alcohol was removed and saponification was complete before the addition of permanganate and nitric acid.

PREPARATION OF ERYTHROSIN

For the preparation of the disodium salt of tetraiodofluorescein, a suspension of the acid in water could be exactly neutralized by the addition of the requisite amount of standard 0.02 *N* alkali and the solution evaporated to dryness. It was found, however, that products obtained in this manner were difficult to get dry and were invariably low in iodine. Sodium carbonate gave us better results, and accordingly the following method was adopted: 3 g. of tetraiodofluorescein and an equal weight of dry sodium carbonate were suspended in 150 cc. of absolute alcohol and, after standing some hours, the whole heated to boiling for a few minutes. The undissolved carbonate was filtered off and the liquid concentrated under reduced pressure until the separation of the salt commenced. The small amount of precipitate was removed by filtration and the evaporation of the solution continued further. When the volume had reached approximately 30 cc., an equal amount of absolute ether was slowly added and crystallization allowed to proceed over night. The red crystals were separated rapidly by filtration, washed with alcohol and ether, and dried in a vacuum desiccator over fresh sulfuric acid. Erythrosin prepared as described contains solvent of crystallization which, however, is not all alcohol, but in part water. The water has partially resulted from the neutralization of the erythrosin acid by the sodium carbonate, and in spite of the fact that the amount of water is exceedingly small as compared with the large amount of alcohol, nevertheless erythrosin takes up that water, so great is the avidity of the sodium salt to form a hydrate. Completely hydrated erythrosin is obtained when the pure sodium salt, freed from alcohol by drying at 130° C., is dissolved in water, the solution evaporated to dryness under reduced pressure, and the dry residue further dried in a vacuum desiccator.

PURE ERYTHROSIN

In the following table are given the results of analyses of several samples. The relative proportions of alcohol and water in erythrosin were obtained as follows: A weighed sample of the salt (3 to 4 g.) was put in a large boat, placed in a glass tube and heated at the desired temperature, a stream of air carrying the vapors into a combustion tube. From the quantities of carbon dioxide and water produced, the relative amounts of the two solvents in the sample of erythrosin can be calculated. All samples, whether from alcohol or from water, were dried, prior to analysis, over sulfuric acid in a vacuum desiccator for 2½ to 3 hrs., which period should be amply sufficient to free crystalline material from any adhering volatile solvent.

These results indicate clearly that erythrosin combines with both alcohol and water. The actual number of mols of each of the two solvents per mol of dye could only be determined approximately, since in the initial stages of dry-

⁸ Chem. Zentr., 1903, II, 69; 1904, I, 609; 1908, I, 2111.

⁹ Chem. News, 103 (1911), 161.

No.	Solvent	Preliminary Drying in Vacuum Desiccator at Room Temp.	Heated Temp. °C.	Hrs.	Loss, Per Cent		
					Alcohol	Water	Per cent
1	Alcohol	10 hrs.	Room	10	1.10	..	..
			120-130	1	7.01	..	..
			130	4	0.09	..	8.20
2	Alcohol	4 days	125	9	2.50	1.02	..
			170	4	0.14	0.39	4.05
3	Alcohol	4 days	170	4	2.85	1.67	4.52
4	Water	2 1/2 hrs.	Room	9	..	1.02	..
			130	1	..	5.23	..
			130	3	..	0.48	..
			160	16	..	0.32	7.05

ing in the desiccator, some of the solvent is undoubtedly lost. Approximately, from water the salt contains: 1 mol erythrosin + 4 mols H_2O ; from alcohol, 1 mol erythrosin + 2 mols C_2H_5O ; from alcohol containing but a very little water, some of each solvent is taken up. But whatever the composition of the hydrated salt, it is obvious that in drying the last portion of the water is retained with extreme tenacity. The question arises—what assurance does one have, outside of the analysis of the dried salt, that all the water has been driven out even when the salt is heated for hours at 160° to 170° C.? May not a state of equilibrium be established at that temperature, wherein liberation of water from the salt proceeds at a very slow rate? Much higher temperatures for drying are inadvisable, for decomposition of erythrosin is likely to set in, evolution of iodine becoming quite noticeable at 200° C. We have analyzed Sample 3 after it had received the treatment described—namely, 4 hrs. at 170° , and Sample 4, which had been dried 5 hrs. at 130° C. and 16 hrs. at 160° C. The results in per cent iodine are:

Sample 3	57.10	56.84	57.01	Av. 56.98
Sample 4	57.20	56.80		Av. 57.00

Calculated for $C_{20}H_{14}O_5Na_2$: 57.70; $C_{20}H_{14}O_5Na_2 + H_2O$: 56.55

That the long heating in the process of drying the two samples at the temperature recorded did not induce decomposition of erythrosin with possible loss of iodine, is evident from the fact that the acid regenerated from the salt was found to contain the right amount of iodine—viz., 60.51 against 60.75 per cent calculated. The conclusion, therefore, seems to be that the low iodine content—approximately 57.00 instead of 57.70 per cent—of our erythrosin, which had been prepared from very pure acid and had been thoroughly dried, must be due to the retention of water by the salt to the extent of about 1.2 per cent (calculated for 1 mol H_2O , 2.00 per cent).

With regard to the manner in which the water is held, little may be said with certainty. In a series of papers from this laboratory, it has been shown that diphenyl fuchsones and many analogous compounds possess the tendency to combine with water and give rise to quinonoid tautomers of the carbinols of varying degrees of stability.

Erythrosin, on the basis of its constitution and in analogy with the other and simpler fuchsones, may act in a similar manner. The constitution of the salt, then, is as follows:

TECHNICAL ERYTHROSIN

A sample of commercial erythrosin acid of reliable manufacture was subjected to the same analysis as our sample which had been completely purified through the diacetate. The acid, upon digestion with alcohol, was found to be practically free from adsorbed iodine. Dried in a vacuum desiccator and for a few minutes at 130° C., it contained 60.61 per cent of iodine against the theoretical 60.75. The acid was converted into erythrosin, in absolute alcohol with sodium carbonate, just as described for our own sample, and the resulting salt was dried in a vacuum over sulfuric acid at room temperature.

(1) One portion of this erythrosin, which had been dried at room temperature for 12 hrs., was heated at 120° to 130° C., and it lost in alcohol and water, during the first hour and a half, 6.27 per cent, and during the next 4 hrs., 0.3 per cent.

(2) A second portion was recrystallized from water, and the sample, after 13 hrs. in a vacuum desiccator, lost at 130° C., during the first hour, 5.65 per cent, and in the next 3 hrs., 0.36 per cent; after that in 16 hrs. at 160° C., 0.09 per cent.

(3) A third portion, from alcohol, lost in 11 hrs. at 135° C., 7.36 per cent as alcohol and 1.36 per cent as water.

(4) A fourth portion, also from alcohol, lost in 4 hrs. at 170° C., 7.57 per cent as alcohol and 1.2 per cent as water. Now, just as in the case of our own erythrosin, this technical product, in spite of the drastic treatment, did not apparently lose all its water. Here again the salt contained less iodine than it should if it were completely dehydrated. Sample 4 gave 57.27, 57.14, 56.92 per cent; average, 57.09 per cent iodine.

CONCLUSION

The conclusion seems justified that the true composition of erythrosin is $C_{20}H_{14}O_5Na_2 + H_2O$, and that it is almost impossible to dehydrate it completely without risk of decomposition of the salt. In view of this, we suggest that the specifications of purity be based upon the following principles: (1) Erythrosin should be dried to approximately constant weight at 120° to 125° C., weighings being made at the end of the second hour and every hour thereafter; it should, then, on solution in very dilute ammonia and careful precipitation, hot, with acetic acid followed by a little sulfuric acid, give 93.5 ± 0.5 per cent of its weight of dry erythrosin acid, after adding a correction of 0.4 per cent for each 100 cc. of water used with a 1-g. sample. This solubility correction was found necessary in experiments upon pure erythrosin acid. (2) The precipitated erythrosin acid should give up no iodine to alcohol, and should, when dry, contain about 60.75 per cent of iodine.

Fire Hazards in Oil Refineries

Fires in oil refineries may be caused by lightning or other mishap, or by carelessness in allowing the oil or vapors to become ignited, states the Bureau of Mines in Serial 2400 just issued. Probably the most frequent cause, however, is the failure of refining equipment. Stills are designed to be safe, and usually are safe. Nevertheless, defects sometimes occur, as in all metal structures, and unless promptly discovered and remedied may result in serious fires and explosions. The dangers of refining crude oil are well recognized, and all modern refineries have developed highly efficient systems of inspection and fire prevention.

Further tests have been conducted at Pittsburgh, Pa., by the Bureau of Mines to obtain data as to the comparative sensitiveness of gasoline vapors and methane with respect to their ignition from electric flashes. This work has a bearing on the degree of protection that will be necessary for electric motors used in and around buildings where gasoline vapor may be present.