manufacture could be completely paralleled. All stages of the work on any given oil had to be checked against authentically pure oils in the soap base. As a standard procedure we have used 1 per cent of each oil properly incorporated in a standard milled base. Samples of such soaps in uniform cakes have been stored under conditions standardized to duplicate commercial conditions and for at least one month. Comparison of the soaps thus prepared and stored have been used as the basis for further developments until final tests have indicated the successful attainment of our goal in each case.

These test bars are identified by numbers, affording no clue to the identity. A fixed testing panel of experienced essential oil chemists and perfumers is used for such comparisons through all stages of the work and a properly weighted summary of opinions and comment is employed for guidance during development stages and for final decision. If a synthetic oil developed in this manner is passed on blind test by such a panel, confidence can then be felt that it is prepared to do the job for which it is designed.

Careful selection of the authentic oil samples is, of course, important and while that represents an entirely different phase of our work it has been accomplished by the use of a trained scientific representative who has visited all regions of the earth in which essential oils or essential oil materials are produced.

Oil of Bergamot furnishes an outstanding example of the importance of this type of work to the soap perfumer. This oil is produced in only a very restricted area on the Italian peninsula and all commerce in this oil between the producing regions and the outside world is completely cut off. It has been possible in this emergency to produce oils not only answering all the analytical requirements of natural Bergamot Oil, but affording practically perfect replacement of it for use in perfumery and even in the flavoring industry. Unfortunately the shortage referred to with attendant high prices has encouraged, as it always does, the hasty creation of so-called synthetic Bergamot Oils frequently deviating greatly from the natural properties of the oil and failing entirely to replace it effectively in an established formula.

Space is not available to include analytical details, but a comparison of a number of oils of this character prepared in our laboratories is available to any who are interested.

In conclusion I would like to say that while the present emergency is responsible for highly intensifying interest in the development of scientific essential oils, it would be a grave mistake to regard these simply as products not altogether up to standard and to be used only in the absence of their natural prototypes. As pointed out, they frequently do a much better job than the latter, are commonly lower and more stable in price and more readily available, particularly where unusual quantities are involved. They are products to be considered at all times and not merely in emergency.

The Colorimetric Determination of Titanium Dioxide in Soaps

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INTRODUCTION:

Titanium dioxide is often added in small amounts to toilet soaps for the purpose of improving color, and a reliable and rapid method for its quantitative estimation is frequently required. Elements yielding insoluble hydroxides in weakly ammoniacal solutions interfere with the determination of titanium by the usual gravimetric procedure of precipitating as the hydroxide, igniting, and weighing as the oxide. Iron and aluminum, which fall in the above category, are commonly present in small quantities as impurities in soaps and can only be separated from titanium by tedious and time-consuming operations.

The colorimetric method for titanium based on the intensity of yellow color developed when hydrogen peroxide is added to a sulfuric acid solution of titanium is much more rapid than the gravimetric procedure, for it possesses the advantage that, with the exception of iron, all metals commonly present in soap are without effect on the color. Iron affects the color to a very slight degree (1), approximately 500 parts of Fe_2O_3 being required to produce a color equivalent to that given by one part of TiO_2. Since the amount of iron in soaps is much less than the titanium dioxide ordinarily added, its effect on the colorimetric estimation of the pigment is inappreciable.

Phosphates affect the color developed by the reagents. Less color is produced by a given amount of titanium dioxide when phosphates are present. Usually titanium dioxide is not found in phosphated soaps. It may be readily separated from phosphates by precipitating the TiO_2 from boiling ammoniacal solutions, filtering, and washing until the precipitated oxides are free from phosphate.

SOLUTION OF TITANIUM DIOXIDE:

In the analysis of soaps, the titanium dioxide which has previously been separated from organic matter by ashing or other means, must be brought into solution by either an acid or alkali fusion. The complete solution of titanium dioxide by fusion with acid sulfates or sodium peroxide, is often difficult to achieve especially if the fusion mixture is heated to a high temperature. Experiments in which eight grams of potassium acid sulfate and 0.2 grams of titanium dioxide were fused under varying conditions indicated that fusion over a low Bunsen flame for forty-five minutes would usually yield clear solutions when the melt was dissolved in 5% sulfuric acid. Fusions made at the full heat of the Bunsen burner were uniformly incompletely soluble even though preceded by a forty-five minute fusion over a low flame. Occasionally incomplete solution was noted even with the low heat, suggesting that the fusion temperature and time are rather critical.

Alkaline oxidizing fusions with sodium peroxide indicated that the temperature of fusion was critical with this reagent also.

A mixture of 20 grams of ammonium sulfate and 20 ml. of sulfuric acid was eventually found to be most satisfactory for solution of the titanium dioxide. The time required to effect complete solution varied from one and one-half hours at the full heat of an electric hot plate to five minutes at the full heat of a Bunsen burner, provided the fusion was stirred thoroughly during the heating period. The fusion mixture was allowed to cool and then diluted with water to yield an acid solution of the titanium. Numerous fusions at the full heat of the Bunsen burner for five to ten minutes resulted in uniformly satisfactory solution, provided the fusion mixture was thoroughly stirred during the heating period. The evaporation of the sulfuric acid apparently serves to properly limit the fusion temperature.

Ammonium sulfate-sulfuric acid fusion was employed both for the preparation of the standard titanium solution and of the solution of the titanium dioxide from the soap.

PREPARATION OF TITANIUM SOLUTIONS FROM SOAP:

Two methods for separating the titanium dioxide from the organic matter were employed. In the first the soap was ignited in a pyrex beaker until no more volatile matter was given off. The resulting charred mass was treated directly with ammonium sulfate and sulfuric acid. This procedure gave satisfactory results, but was not preferred because the carbon residue darkened the fusion so that the point of complete solution of the titanium dioxide was obscured.

In the second method, titanium dioxide was separated from the soap by alcohol. The soap was dissolved in 95% alcohol, and the titanium and other alsohol-insoluble materials were filtered from the solution and washed well with portions of hot alcohol. The filter paper containing the residue was then readily ashed in a pyrex beaker without leaving any appreciable carbon residue. When this material was fused with ammonium sulfate and sulfuric acid, the point of complete solution of the titanium dioxide was clearly visible. The latter procedure has been found applicable to all titanium dioxide-containing soaps thus far encountered.

STANDARD TITANIUM SOLUTION:

The standard titanium solution for color comparisons was prepared by fusing 0.2 g. of titanium dioxide, 20 g. of ammonium sulfate, and 30 ml. of concentrated sulfuric acid in a 200 ml. pyrex beaker. The mixture was heated with stirring over a full Bunsen flame until a clear solution resulted. After cooling to room temperature the solution was transferred to a 500 ml. volumetric flask and made to volume with distilled water. The strength of the standard solution was checked by taking a 50 ml. aliquot, diluting to 150 ml. with distilled water, heating to boiling, and making slightly ammoniacal with 1:1 ammonium hydroxide to precipitate the titanium as the hydroxide. The solution was allowed to stand 20 minutes on the steam bath to complete the precipitation. Then the precipitate was filtered, washed well with hot water, and subsequently the paper and precipitate were ignited to constant weight over a Meker burner. The residue, minus the weight of the filter paper ash, was taken as titanium dioxide.

ANALYTICAL PROCEDURE:

A sample of soap containing .0002 to .004 g. of TiO_2 is weighed into a 200 ml. pyrex beaker and approximately 120 ml. of neutralized 95% alcohol is added. After boiling for three minutes, the insoluble portion is allowed to settle, and the clear liquor is decanted through a filter paper. The residue is again digested with alcohol and finally transferred to the filter paper by means of alcohol. Occasionally the first few ml. of the filtrate are cloudy and must be returned to the paper to secure complete clarity. After washing the residue well with hot alcohol, the filter paper is placed in the original beaker and ashed over a Bunsen flame. It is not necessary to remove the last traces of carbon resulting from the paper, since it is filtered out later. Twenty grams of ammonium sulfate and 20 ml. of concentrated sulfuric acid are added to the beaker, and with constant stirring, the mixture is heated with the full heat of a Bunsen flame for 5 to 10 minutes until the titanium is completely in solution. After cooling, the solution is diluted and filtered into a 250 ml. volumetric flask. The beaker and filter paper are washed well, and the filtrate is made to volume with distilled water. Fifty ml. of the well-mixed solution are pipetted into a 100 ml. Nessler tube. Five ml. of 3% hydrogen peroxide and 8 ml. of 1:1 sulphuric acid are added, and the solution is diluted to the mark. It is necessary, according to most investigators, to have at least 5% of sulfuric acid present to prevent the formation of meta titanic acid which does not give the yellow color with hydrogen peroxide. About 75 ml. of distilled water, 10 ml. of 1:1 sulfuric acid, and 5 ml. of 3% hydrogen peroxide are added to another Nessler tube, and after mixing, standard titanium solution is added volumetrically until the color equals that in the sample tube. Before adding the final drops of standard titanium solution, distilled water is added to equalize the length of the two columns.

CALCULATION:

$$\frac{C \times S \times 100}{W} = \%\ TiO_2$$

where, C = ml. of standard titanium solution
S = gms. of TiO_2 per ml. of standard titanium solution
W = weight of sample represented by aliquot

RECOVERY OF TiO_2 ADDED TO SOAP:

As a means of checking the accuracy of the method, known amounts of titanium dioxide were added to soap chips, and the mixtures were analyzed. Table I gives typical results.

TABLE 1

% TiO_2 Added	% TiO_2 Determined
0.100	0.108
0.100	0.112
0.200	0.210
0.200	0.202
0.300	0.312
0.300	0.304

The procedure has been employed for a considerable period by a number of analysts in different laboratories, and experience has indicated that the manipulations are simple and the results trustworthy.

REFERENCE

(1) Snell. Colorimetric Methods of Analysis—D. Van Nostrand, 355, 1936.