Modern Methods for Replacement of Essential Oils in the Soap Industry

By L. E. YOUNG

FRITZSCHE BROTHERS, INC., NEW YORK

IN THE early days of the soap industry only natural materials, such as essential oils or other materials extracted from vegetable and in some cases animal products, were available. However, with increasing knowledge of essential oil constituents and the subsequent synthetic preparation of many of these on a commercial scale, there have been made available to the soap perfumer very valuable and at the same time very economical means for supplementing and reenforcing these natural products.

The synthetic aromatic chemicals possessed the advantage of greater economy, uniformity and dependability of supply. Unfortunately these advantages caused many perfumers to overlook the fact that whereas many of the main constituents of essential oils had been identified and prepared synthetically, there were numerous others still not identified, often of great complexity, and which were very important in the final odor effect and stability of the essential oil complex when used in soap. As a result the use of such aromatics was frequently carried to extremes with neglect of the natural essential oils and with results rather disastrous to the odor quality and stability in soap. This tendency has been even more marked when certain essential oils were scarce or high in price. As noted essential oils are in general rather complex in their composition and consist usually of an aggregation of chemical compounds covering a wide range as regards volatility. To achieve odor effects similar to those imparted by essential oils it is necessary to attain this same range of volatility. This is very difficult to obtain by simply combining the aromatic chemicals available, because while these may permit the formulation of compounds superficially resembling the essential oils in odor, they do not stand up in soaps.

Even in normal times it is highly desirable from the standpoint of economy to bring about replacement of essential oils with products which can be prepared more or less independently of natural sources. It is seldom that this goal can be attained one hundred per cent, but even where recourse must be had to natural products, the available supply of these may be greatly stretched without loss of efficiency by their scientific combination with various synthetic ingredients.

As a result during the past several decades, and more particularly within the last few years, the essential oil and aromatic industry has made great progress in the development of what might be termed most correctly as synthetic essential oils. Those of real merit, and there are many of them, have been developed on a really scientific basis, beginning with identification and quantitative determination of as many of the natural occurring ingredients as possible. This had to be followed by the synthesis of the most essential of those not already available in commerce. At this point the perfumer's art, based on experience and long study of all the aromatic materials available for perfumery, has had to supplement the science of the organic chemist by determination of odor relationships on which the replacement of materials or effects not identified chemically or not available commercially could be accomplished.

By this combination of art and science it has been possible to produce a great many excellent replacements of natural essential oils, ofttimes meeting complete analytical requirements of the latter. This latter has been in a sense unfortunate because it has created the temptation of offering them for what they were not, namely, as pure oils instead of synthetics. In fact, many such compositions have been prepared with principal thought directed towards duplication of analytical contents and with odor content and value merely secondary.

As a result of this, so-called synthetic oils have come to be regarded by many soap perfumers as necessarily inferior, as in fact many of them were. On the other hand, however, such synthetic oils properly developed on a scientific basis with due regard for their final behavior in soap are in many cases far superior to the natural oils in odor quality and content, and more particularly in stability. It is just another instance of art and science improving on nature as they have done in many other fields.

In the development of a perfume composition the perfumer does not normally restrict himself to the use of either natural or synthetic ingredients, but uses what comes to hand to achieve the result desired. Accordingly many formulas based on such indiscriminate combinations are established in use and it is desirable and frequently necessary that the perfumer be provided with effective duplications of ingredients, principally natural essential oils, which are no longer available due to disruption of commerce by war, as is the case today, but not infrequently from other causes.

I have before me a list of about fifty common essential oils which are regularly available in the form of effective synthetic replacements. Perhaps one-half of these are of outstanding interest to the soapmaker and I mention as a few of the most significant such oils as Bergamot, Cassia, Citronella, Geranium, Lavender, Rosemary, Sandalwood, Vetiver and Ylang Ylang. Others are constantly being developed as need arises.

Such oils must be sharply and clearly distinguished from perfume compositions bearing the names of these oils but usually prepared with no view to the actual replacement of the oils themselves. These are in reality nothing but finished perfumes and could not be considered as replacements of the natural oils in an established formula. Care must be taken also not to place complete reliance on analytical specifications which after all do not show up in olfactory examination. The important things are that the oil shall compare favorably with the average oil which is used in its odor quality and content, not only in its original form but when combined with the other ingredients of the formula and introduced into the finished product.

In our development work along these lines we have found absolutely essential the maintenance of a small pilot plant in which the conditions of commercial soap

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

By L. B. PARSONS and F. A. VAUGHAN
LEVER BROTHERS COMPANY, CAMBRIDGE, MASS.

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