

ments will undoubtedly take place in the application of spectrophotometric and chromatographic methods to essential oil analysis.

Only when the analyst is absolutely satisfied of the authenticity of the sample under examination should he be inclined to pass an "abnormal" oil for submission to subjective tests. Oils from sources of supply of new geographical origin come into this category, as well as those produced by the employment of modern distillation units in place of "peasant" stills.

Brazilian rosewood, sassafras, and dementholised mint oils may be cited as important newcomers to the essential oil markets in recent years, while the controversy over otto of rose in the years immediately before the War is an excellent example of the influence of equipment on the characteristics of an essential oil. Guenther, *op. cit.*, Vol. V, p. 3, *et seq.*, gives an admirable survey of the otto of rose question.

Subjective tests on the odour, and, where necessary, flavour, of the essential oil then follow, comparison being made with standard samples kept under proper conditions, followed by trial formulation in which the new oil is incorporated in place of the previously accepted delivery. Standard samples should be kept in small well-filled amber glass bottles, preferably closed with glass stoppers, or alternatively tinfoil-wrapped corks, in a dark cupboard at a uniformly cool temperature. Under such conditions deterioration of sensitive oils, such as those from citrus fruits, is likely to be inappreciable over many months.

LIPSTICKS—THEIR FORMULATION, MANUFACTURE, AND ANALYSIS*

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HERE ARE TWO lipstick formulas—one a "creamy" and one a "high stain."

The castor oil is used as the main vehicle for the color and as a partial solvent for the halogenated fluorescein termed "bromo acids." The isopropyl myristate acts to break the viscosity of the castor oil and allow better contact with the lip. The lanolin is used for its emollient properties and for a degree of tackiness and drag. The wax phase is balanced to utilize

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	Creamy	High Stain
Castor oil	65	60
Propylene glycol monoricinoleate	...	10
Lanolin	10	5
Isopropyl myristate	5	...
Polyethylene glycol 400	...	5
Beeswax	7	7
Candelilla wax	7	7
Ozokerite	3	3
Carnauba wax	3	3
	100	100
Propyl <i>p</i> -hydroxybenzoate	0.2	0.2
Halogenated fluorescein	3	3
Certified lake colors	12	12

the toughness of ozokerite, the high melting point of carnauba, the hardness and thinness of candelilla, together with the resiliency of beeswax. A certain degree of insolubility of the waxes in the oil is desirable, too, for a continuous system rather than that of complete mutual solubility. Complete solubility results in a mushy soft product due to mutual melting point depression effect.

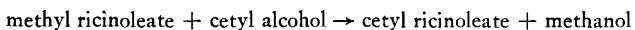
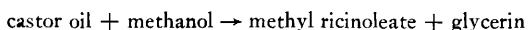
The high stain sticks employ a solvent—in this instance polyethylene glycol 400. The polyethylene glycol is not soluble in castor oil. Propylene glycol monoricinoleate acts as a mutual solvent or coupling agent. To vary the properties of these lipsticks, changes in the proportions of the ingredients can be made. However, we are by no means limited to these materials. Partially hydrogenated vegetable oils can be used in securing creaminess. Completely hydrogenated castor oil, melting point 82°C., is an excellent stiffener and raises the melting point of the product. Spermaceti, cetyl, and stearyl alcohols also find a place in formulations.

Various derivatives of lanolin are also employed. Acetylated lanolin is more soluble in castor oil than is lanolin. Lanolin oils, which are solvent extractions of lanolin, eliminate much of the tack of the lanolin. Isopropyl alcohol cross esterification products of lanolin are liquids and have less of the tack of lanolin. These products, however, must be considered as a physical mixture of unreacted lanolin, isopropyl ester of lanolin fatty acids, and free lanolin alcohols.

Polyethylene glycol derivatives of lanolin are generally water dispersible and as such are not satisfactory. Products with a shorter chain length would in all probability be satisfactory. Physical mixtures of lanolin alcohols or sterols together with lanolin, mineral oil, and petrolatum marketed as absorption bases are being used successfully in lipsticks. Consideration must be given to their hydrocarbon content.

Isopropyl myristate was mentioned as an agent to break the viscosity of the castor oil. There are a number of materials that fall into this cate-

This is indicated by a rather rapid decrease in its acid number. In preparation of esters this reaction goes on to a considerable degree as a side reaction. The hydroxyl group does oxidize to form heptaldehyde. Even traces of heptaldehyde are sufficient to make the product unusable for lipsticks. Quite often ricinoleates have not been fully explored because of these impurities. We use an indirect method to form the ricinoleates to avoid cross esterification. Care in selection of the catalyst and operating conditions avoids the formation of aldehydes and other odoriferous by-products. The lower aliphatic esters are made by alcoholysis of the glyceride. The other esters are then made by replacement of the lower alkyl radical with the desired alcohol.



We have prepared a number of ricinoleate esters using these methods. The ethyl and isopropyl as well as the propylene glycol monoester have been mentioned previously. Cetyl and stearyl ricinoleate are liquids with melting points of 20 and 25°C. They are somewhat less viscous than castor oil. They are completely compatible with castor oil and can be used as a substantial replacement of it. The ricinoleates of lanolin alcohols and lanolin sterols are viscous products with exceptional emolliency. We are also making the corresponding oleates. The properties are somewhat the same for the entire series with the exception of having less body and being poorer solvents for bromo acid.

The term solvents has been used several times. There are materials that are excellent solvents for bromo acid but are of limited value as they do not allow the dye to stain the skin. Polyethylene glycol ether of lauryl alcohol is a representative case. Where reference is made to a solvent, we mean one that not only dissolves the bromo acid but assists it in staining the skin. The solvents used in the high stain lipsticks fall into two groups: the free glycols or polyglycol esters and fatty acid esters of the polyglycol ethers. Of the glycols, propylene and butylene are most frequently used. The polyethylene glycols up to a molecular weight of 1000 are effective. Consideration must be given to the hygroscopic effect of these materials. Due to the anhydrous nature of a lipstick, moisture is drawn from the lips in order to establish a hygroscopic equilibrium, where these materials are used. This can result in dry, parched lips. We know of no miracle ingredient, with one exception, which will offset this hygroscopic effect. This ingredient is water, which is incompatible with the general type of lipstick. As the molecular weight increases, the hygroscopic effect decreases but so does the staining power of their solutions. The polyethylene glycol monoesters of lauric, palmitic, stearic, oleic, and ricinoleic acids are good solvents. There is a tendency for the longer polyglycol chain esters to act as emulsi-

fiers or water solubilizers. The use of tetrahydrofurfuryl acetate as a bromo solvent is covered by patents.

As staining colors the halogenated fluoresceins are used:

Color	Chemical Formula	Stain
D&C Orange #5	Dibromfluorescein	Orange red
D&C Red #21	Tetrabromfluorescein	Red
D&C Red #27	Tetrabromtetrachlorfluorescein	Blue red

There are several other colors of this general structure that are certified. Their use has been limited. General practice is to use 3 parts bromo acids and 12 parts lake color to 100 parts base.

Variation in consistency and melting point in different shades of lipstick is quite often encountered even though the same base and color concentration are used. This is due to differences in the oil absorption of the various colors. Taking an arbitrary oil absorption as indicated by flow characteristics as a value of 0, we have charted the colors as follows, giving a negative value to those with a lesser amount of oil absorption and a positive value to those with a greater amount.

D&C Orange #4	- 2.0
D&C Red #9	- 3.0
D&C Red #35	- 0.5
D&C Red #21 Al. salt.....	15.0
D&C Red #11	3.5
D&C Red #13	- 1.0
D&C Red #19 Al. salt.....	1.0
D&C Red #7	0.5
D&C Red #34 Resinated Ca. salt.....	12.0
Titanium Dioxide	- 4.0
D&C Red #21	- 2.5
D&C Orange #5	- 1.5
D&C Red #27	- 2.0

The weighted average of oil absorption for each formula in a series of shades should be as uniform as possible. The differences in oil absorption are apparent where melting points are taken by the capillary tube method. A lipstick made with a colorless base with 65°C. m.p. might have a m.p. of 66° in a shade high in titanium dioxide and 72°C. in a shade high in D&C Red #34.

In manufacturing lipsticks, the colors are mixed with part of the oil in change can mixer A, then passed through a three-roller mill B. The color and oil are ground a sufficient number of times to achieve a color distribution of 7 or better on a grind gauge. The color in oil is heated to 70°C. in kettle C. The balance of materials is heated to 90° in kettle D. The contents of D is strained through a 250-mesh stainless steel screen E into C with constant agitation in C. After several hours' stirring, samples are drawn off for control tests. Any adjustment in shade is made by using color bases

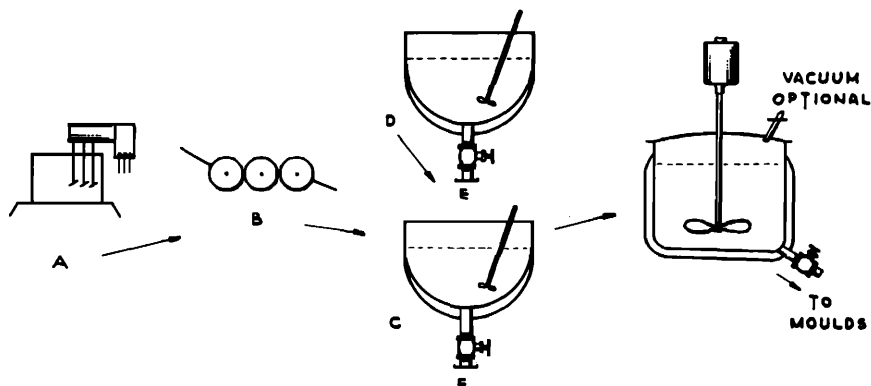


Figure 1.

of the same concentration of color and bromo acid as are used in the lipstick. If satisfactory, the lipstick is drawn off from C through a 200-mesh stainless steel screen F ready to mold or slabbed for future molding. Prior to molding the material is melted with slow agitation in melting kettle G to remove entrapped air. A vacuum in a closed melting kettle will greatly aid in eliminating entrapped air. Temperature control is important throughout the processing, with care being taken to avoid excessive temperatures in the kettle.

CONTROL METHODS

Control in manufacturing lipsticks is greatly assisted by a thorough control of incoming raw materials. Methods for raw material control are covered by the Toilet Goods Association, American Oil Chemists Society, and Association of Official Agricultural Chemists. Melting points are taken by the capillary tube method. The results secured are relative but should be consistent for the same color formulation. This method depends on "flow" and differences in oil absorption of the various coloring matters will give different melting points. A substantial difference in melting point for a given shade indicates some error in the formula or in the raw materials. Heat resistance for a minimum period of 24 hours is a much better guide of heat stability. Lipstick A is inserted in case B and passed through bar C, to hold it in vertical position. It is kept in a constant temperature box at a temperature of 55°C. or any other desired temperature for 24 hours. Any tendency to droop or distort is noted. The stick should not show any change after 24 hours at the desired temperature.

Hardness is tested by pouring lipstick into a ring 2 in. inside diameter and 1 in. deep. It is allowed to stand for 12 hours in a constant temperature box at 20°C. Tests are taken with a penetrometer (A.S.T.M.). Five

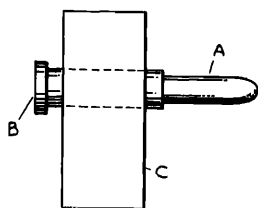


Figure 2.—Heat Test: A = Lipstick, B = Lipstick Holder, and C = Stationary Block.

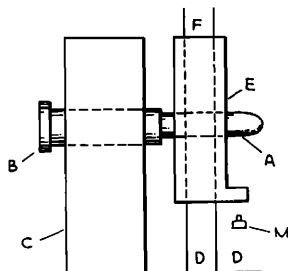


Figure 3.—Rupture Test: A = Lipstick, B = Lipstick Case, C = Stationary Block, E = Movable Block, D = Guide Rack, and M = Micro Switch.

readings are taken. The average is calculated and compared with standard.

High humidity tests are run by putting filled lipstick containers in a desiccator containing water. The desiccator is kept in a constant temperature box at a temperature of 45°C. and examined periodically. The stick is examined for sweating and bleeding. The container is examined for discoloration or corrosion.

RUPTURE TESTS

Lipstick A is put in holder B and inserted into stationary block C and through movable block E. Block E rides on guide rods D. Weights are put at F, with a 30-second interval between each addition of weight. When stick ruptures, E moves on guide rods D to reach microswitch M, which lights up bulb. Weights plus weight of E is pressure required for rupture.

Shade and intensity of stain are best judged on the skin by comparison with standard. Skin tone and undertone are also checked on the skin. Mass tone is judged by comparison with standard.

Color content is determined by extraction with isopropyl ether. The ether solution is washed several times with 0.1 *N* aqueous sodium hydroxide. This will extract the bromo acids. The sodium hydroxide extraction is precipitated with 1 *N* hydrochloric acid. The reconverted bromo acids are washed several times with the hydrochloric acid. They are dried at 80°C. and weighed. The bromo acid content of any bromo acid lakes will also be extracted under these conditions. The residue from the ether extraction is washed several times with isopropyl ether. It is air dried in a hood and weighed to determine insoluble coloring matter.

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