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Abstract

It is now possible to formulate lipsticks with a minimum number of ingredients. By using isostearyl alcohol as the oil phase and the appropriate vicinal glycols as the wax phase, both of which are good bromo solvents, a wide range of plastic properties may be obtained. The necessity of using oxidation inhibitors and couplers for incompatible bromo solvents is avoided. These raw materials are colorless, nearly odorless and tasteless, nontoxic, nonirritating, oxidation-stable, miscible with waxes, and are good emollients.

Introduction

I T IS THE PURPOSE of this paper to suggest a means of simplifying lipstick formulation by the use of two new raw materials: isostearyl alcohol and terminal vicinal glycols.

Lipstick formulation has always been a difficult and complex task because of the many aesthetic, physical and chemical requirements the public demands in a lipstick. The number of performance tests which a lipstick must pass is equalled by few other cosmetic products. In an effort to attain the best possible product, formulas usually become quite complicated, containing 15 or 25, or an even larger number of ingredients.

Recently, there has been interest in simplification of this unnecessarily complex technology. Maruszewski has decribed a system of approaching lipstick formulation logically by considering each ingredient as it relates to others by a common property such as consistency (1). This results in better control of the properties of the penultimate formula since the effect of each ingredient is understood. For example, to decrease the consistency, one could decrease the concentration of the ingredient contributing most to that property, meanwhile keeping in mind the effect of this decrease on the other properties of the lipstick; these effects are known from a study of the type just described.

Materials, Methods and Procedures

Bromo Acid Solvency

The reason many lipstick formulas are so complex is that raw materials which perform one function well, such as solvency for dyes, can lack an essential property such as solubility in the rest of the lipstick composition. One property a lipstick pomade must have is solvency for tetrabromofluorescein, known in the Trade as bromo acid or bromo. Bromo and the other halogenated fluoresceins produce the stain on the lip. Propylene glycol is an example of a material with such antagonistic properties. It is a solvent for bromo, but its use in lipsticks is limited because it is water-soluble and hygroscopic and is not soluble in oils and waxes. If propylene glycol is used, other materials must be added to the formula to solubilize it (2). The solubilizer may affect the consistency so that the wax phase must be increased, and so on.

In this way, the formula becomes more and more complicated as small amounts of various materials are added, each to overcome some deficiency of another.

Achieving a lipstick base with good solvency for bromo has always been a problem. Twenty years ago, Henri Coutinho, in a masterly study entitled, "Molecular Constitution and Bromo Acid Solubility," stated :

"The problem of finding a satisfactory solvent for bromo is indeed a highly important one. Bromo, up to now, has been the only satisfactory dye to give the so highly-desired permanent stain on application of a lipstick still true. It is therefore of extreme importance to develop a solvent, specially designed and streamlined, so as to bring out the desired staining properties as strongly as possible (3)."

The compound which Coutinho concluded would be an ideal bromo solvent was a benzyl polyglycol ester of an unsaturated dihydroxy fatty acid, which contains all the characteristics and functional groups Coutinho found to contribute bromo solvency to a molecule.

A lipstick is thought of as consisting of an oil phase to which a wax phase is added to produce a solid. Formulation has always been complicated by the necessity of using, on the one hand, a good solvent for bromo in the oil phase and, on the other, nonsolvents such as carnauba wax and beeswax to solidify the bromo solution. Many liquids have been used as bromo solvents but all of them have had disadvantages, e.g., castor oil (high viscosity), oleyl alcohol (oxidation), tetrahydrofurfuryl acetate (taste, irritation), hexadecyl alcohol (poor solvent). Others are water-soluble and have the same disadvantage as propylene glycol mentioned previously.

All the solid materials used for the wax phase, beeswax, carnauba, candellila, ozokerite, ceresin, paraffin, have been poor bromo solvents. Solids which are good bromo solvents are water-soluble, e.g., polyethylene glycols.

We have found that the aliphatic vicinal glycols with chain lengths from $C_{11}-C_{20}$ are excellent bromo solvents and have none of the disadvantages just mentioned. Isostearyl alcohol, we will see, is as good a bromo solvent as oleyl alcohol and is nonoxidizing. The preparation of these compounds is outlined in Table I.

Several investigators have outlined the requirements for an ideal bromo solvent (2,4,5). Coutinho lists eight points as follows:

1) As little odor as possible, so as to avoid the necessity of adding high percentages of perfume oils, many of which display some irritating qualities, and at the same time to keep the cost down.

2) No taste; it should not be bitter or astringent. 3) It must not turn rancid on standing or with the addition of bromo, as eastor oil does; this again will result in cutting down the percentage of perfume oils.

4) Miscible with the usual cosmetic materials to avoid sweating out and change in texture.

5) No toxic and irritating properties.

6) No low boiling point, therefore no evaporation and resulting shrinkage, which in turn would affect the strength of the finished stick.

¹ Presented at the AOCS Meeting Chicago, October 1967.

Chemistry of the	TABLE Fatty Glyco	I ls and Isostearyl Alcohol
Terminal Vicinal Glycols		
CH3(CH2)xCH = CH2 alpha olefin	[0] ————————————————————————————————————	O CH3(CH2)xCHCH2 olefin oxide
O CH ₃ (CH ₂) _x CHCH ₂	$\xrightarrow{H_2O}$	OH OH CH3(CH2)xCHCH2 terminal vicinal glycol
Isostearyl Alcohol CH3		CH3
CH ₃ (CH ₂) ₁₄ CHCOOCH ₃ (and other methyl- branched isomers)	[H] →	CH ₃ (CH ₂) ₁₄ CHCH ₂ OH + CH ₃ OH isostearyl alcohol

7) If possible be emollient, but in no case drying on the lip tissues.

8) It should give to the mass the important property of leaving on the lips a non-greasy, not too heavy film, satisfactorily rub-proof or wipe-proof.

The melting point of the fatty glycols can be varied over a wide range by varying the molecular weight. Thus, a lipstick can be formulated over a wide range of plastic properties, using the fatty glycols as the waxy component, without reducing the bromo solvency as the natural waxes and paraffins do. Indeed, we will see that solvency of such formulas is enhanced. The staining properties of lipsticks made in this way are excellent. The glycols are colorless, have a mild fatty odor and taste, do not oxidize, are nontoxic and nonirritating, are good emollients, and form an unusually persistent water-proof film on the skin. In short, they meet all Coutinho's requirements for an ideal bromo solvent.

Isostearyl alcohol is also colorless, odorless, does not oxidize, and is nontoxic and nonirritating. It is an ideal replacement for castor oil and oleyl alcohol for the oil phase.

Both the glycols and isostearyl alcohol are mutually soluble in all the common lipstick ingredients we have tested, including carnauba, candellila, ozokerite, beeswax, castor oil, oleyl alcohol, isopropyl myristate, etc.

The solvency for bromo of a large number of materials was determined by keeping them in contact with solid tetrabromoflurescein for one week at 65 C, shaking every day. The bromo content of the supernatant liquid was then determined by diluting a sample in acidified alcohol, and measuring absorption at 477 m μ .

We found that it is important to keep these solutions in the dark until the last possible moment. For example, bromo-saturated oleyl alcohol measured immediately after being taken from the aging oven gave a bromo content of 0.20%, whereas one allowed to stand for an afternoon on the desk gave 0.005%. When samples are protected from the light, results are reproducible $\pm 10\%$. Table II shows the solvencies of a number of liquids as determined by this method.

It can be seen that isostearyl alcohol is comparable to oleyl alcohol as a bromo solvent but not as good as castor oil. However, its low viscosity and freedom

TABLE II

Liquids—Bromo	Solubility
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Solvent	% Bromo		
White mineral oil	0.1		
Isopropyl palmitate	0.1		
Isopropyl palmitate Hexadecyl alcohol	0.1		
Olevl alcohol	0.25		
Isostearyl alcohol	0.27		
Propylene glycol	0.40		
Castor oil	0.48		

TABLE III

	_		
Solvent	mp C	% Bromo	
Carnauba wax	82	<0.1	
Ozokerite	85	< 0.1	
Beeswax	63	<0.1	
Cetyl alcohol	49	0.20	
C11-14 terminal vicinal glycol	46	0.60	
C15–1s terminal vicinal glycol	64	0.85	

from rancidification make it preferable as a lipstick material. An odor comparison test easily reveals the superiority of isostearyl alcohol even to fresh samples of oleyl alcohol.

The bromo solvency of castor oil as reported in the literature varies widely. Coutinho found that different samples of bromo gave different solubilities in castor oil, from 0.2% to 1.7%. This seems to indicate that something other than true molecular solution is involved in bromo solubility. There is evidence that bromo is dispersed in these solvents as a colloid. All these solutions show a strong Tyndall effect which increases with concentration. We compared four new samples of commercial, certified bromo by our method and found no difference in solubility among these different samples. Table III shows the solvencies of a number of solid materials, as determined by our method.

It can be seen that the bromo solvencies of the terminal vicinal glycols are slightly higher than, but in the range of, castor oil. Again, terminal vicinal glycols are waxy materials, colorless, nonoxidizing, nontoxic, and nonirritating, and have a mild, fatty odor and taste. They are mutually soluble in all the oil phase ingredients just mentioned and all the common waxes: carnauba, beeswax, ozokerite, etc. The glycols are also good emollients, they leave a tenacious, water-proof film on the skin.

Lipstick Formulation With Fatty Glycols and Isostearyl Alcohol

Isostearyl alcohol is available from Ashland Chemicals under the Trade name Adol 66. Two fatty glycols are also available from Ashland: C_{11-14} terminal vicinal glycol has been named Adol 114 and the C_{15-18} terminal vicinal glycol named Adol 158.

In order to realize the unique advantages of isostearyl alcohol and the fatty glycols in lipsticks, we prepared some very simple formulas, consisting of a single ingredient in the oil phase and a single ingredient in the wax phase. These formulas are shown in Table IV. Adol 66 was compared to castor oil as the oil phase, using three different wax phases: Adol 158, carnauba wax, and beeswax. Two per cent bromo was added to each formula, mixed 16 hr at 70 C, and cast into sticks.

The staining power of each stick was evaluated subjectively by applying it to the forearm and noting

TABLE IV Simple Lipstick Pomades^{a,b}

	%						
	A	В	C	D	Е	F	
Isostearyl alcohol	40		74		55		
Castor oil		50		80		70	
C15-18 terminal vicinal glycol	60	50					
Carnauba wax			26	20			
Beeswax					45	30	
			·				
Total	100	100	100	100	100	100	

^a 2% D&C red no. 21 added to each of above formulas. ^b Staining power: A > B > C > D = E = F. how quickly the stain developed, its intensity, etc. The results are shown at the bottom of Table IV. Isostearyl alcohol proved more effective than castor oil, and Adol 158 markedly enhanced staining power. Not shown is the remarkably fast stain development exhibited by the fatty glycol formulas.

The Adol 66/Adol 158 stick (A), we believe, represents the ultimate in high-stain lipsticks.

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