

MILK WHITE APPEARANCE AND ITS SIGNIFICANCE IN COSMETIC EMULSIONS

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The factors governing milky white appearance are elaborated and shown to be closely connected with emulsion stability.

AN ATTRACTIVE appearance in a cosmetic emulsion is as desirable as adequate stability, performance and a pleasant odour. The important factors in emulsion stability are : sufficient emulsifier of the correct type, fine particle size and correct phase-volume ratio. Foremost among properties of appearance is a milky whiteness. "Milky-white" has for ages been the sign of purity. In this article we wish to point out that a milky-white appearance in cosmetic emulsions is closely associated with the factors responsible for the stability of the emulsion.

Animal and vegetable milks are typical examples of the way in which Nature makes use of emulsions. The emulsion is the most logical form of the transportation of fatty substances within the aqueous environment of the living cell. The finely dispersed fat droplets form the internal phase of the thin milk emulsions. In this way the resorption and digestion of fatty bodies by the organism is well facilitated. There are other circumstances which justify the existence and use of emulsions. Man and animal alike need three basic food elements : carbohydrates, proteins and fats, and, in addition, water, various salts and vitamins. Natural milk is the ideal mixture of these hydrophylic and hydrophobic food elements. Taking into consideration the foregoing properties of milk, one can summarise the advantages of an emulsion as follows :

1. The possibility of combining the various hydrophylic and hydrophobic materials in one uniform liquid or cream emulsion.
2. The possibility of regulating the consistency of the emulsion according to any requirements.
3. The dilution of otherwise too concentrated an ingredient, e.g., fats.

In preparing an artificial emulsion one often keeps in mind the requirements of a natural emulsion. In general, one does not limit oneself to the low concentration and small particle size of natural emulsions : one seeks to achieve a more concentrated emulsion of uniformly dispersed particles and of long shelf life.

OPAQUE APPEARANCE

It is rather strange that an emulsion possesses a milky whiteness in spite of the fact that both phases are transparent and colourless. How can we

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explain the fact that a mixture of two transparent substances such as water and oil, form an emulsion which appears milky-white? It appears to be a physical phenomenon. It must be of great interest to the cosmetic manufacturer to determine the causes of opacity and to apply this knowledge to the manufacture of his own preparations.

Colour is an optical property of each and every material, whilst opacity is only the optical property of emulsions. The opposite of opacity is transparency, and we can prepare a range of emulsions which vary between these two extremes. The colour of any substance can be determined by colorimetric methods, by means of instruments such as colorimeters, chromometers, tintometers, etc. Although opacity cannot be measured in this way, I will mention something about refractometers or the idea of refraction. From an optical viewpoint, there is an obvious difference between transparent and opaque dispersion, and this is manifested by the behaviour of the passage of light. A transparent substance will allow the transmission of light with little opposition, but an emulsion forms a definite obstacle. The opaque emulsion will in fact reflect the light due to the different optical properties of the ingredients of the emulsion.

Light travels at a speed of 186,000 miles per second in a vacuum, but much more slowly in water and still slower in oils and fats. The ratio between velocity of light in a vacuum and velocity in any other medium is called *Refractive Index* of the medium. In industry the refractometer is used to determine the refractive index of various commercial products. This provides a rapid and easy method of identifying the purity of oils, fats, waxes, fatty acids, etc. Below is a table of refractive indices of emulsion constituents of interest to the cosmetic industry :

Materials	Refr. indices	Materials	Refr. indices
Vacuum	1.0000	Olive oil	1.469
Air	1.0003	Castor oil	1.478
Water	1.3300	Almond oil	1.471
Methylalcohol	1.329	White mineral oil	1.475
Ethylalcohol	1.362	Glycerin	1.47
Isobutylalcohol	1.3900	Benzene	1.50
Kerosene	1.4500	Gelatine	1.54
Japan Tallow	1.458	Woolwax	1.48
Coconut oil	1.449	Paraffins	1.42
Cacao Butter	1.457	Beeswax	1.44
Palm-nut oil	1.451	Carnauba wax	1.39
Palm oil	1.454		

An emulsion is a two-phase system in which each phase may contain several ingredients. When a beam of light passes at an angle from a phase having a lower refractive index (water-phase) into the oil-phase having a

higher refractive index, the light changes in velocity, i.e., it is refracted. In addition, a certain amount of light will also be reflected. The reflection occurs at the interface between the two phases. *The phenomenon of diffuse reflection is the cause of opacity.*

Now the greater the distance between the refractive indices of the two phases, the greater will be the opacity of the emulsion. It can be anticipated and indeed confirmed by practical experiences that a large amount of glycerin in the aqueous phase will cause a decrease in opacity. Glycerin itself possesses a high refractive index and the water-phase containing it will therefore be of higher refractive index. The result is that the refractive indices of the two phases are now closer to one another.

In an O/W emulsion, for instance, there is an immense number of oil droplets finely dispersed in the external aqueous phase. Light will meet with opposition to its passage from individual oil droplets and it strains to penetrate deeper and deeper through the mass of droplets. As light impinges on an emulsion droplet, only a very tiny proportion will be reflected, the majority of the light continuing deeper into the emulsion. On its way, the light strikes a multitude of droplets of the internal phase until at a certain stage there is a total reflection, i.e., full opacity is developed.

A transparent emulsion on the other hand occurs if the refractive indices of the two phases are identical or very close together. Moreover, the development of the opacity may be caused by other factors. A concentrated emulsion with an internal phase of over 50 per cent, that is, high phase-volume ratio, appears extremely opaque. This is because the particles are close together. In very dilute emulsions, that is, low phase-volume ratio, there exists only relatively few droplets and these are separated by considerable distances. On its way, the light meets only a small number of droplets and therefore a heavier layer of emulsion will be necessary to reflect all the light. It is also possible to realise the higher degree of opacity with favourable conditions such as an increased degree of dispersion. Dispersion aims at breaking the cohesive forces that keep the larger particles together. Such an object can be attained either by mechanical or chemical means or a combination of both. The chemical method depends upon the use of suitable and sufficient emulsifiers. Mechanical dispersion may be brought about by the use of the colloid mill or homogeniser. If we use in an emulsion two phases whose refractive indices are fairly close together, we are left with two opportunities to correct or improve the opacity of that emulsion. These are :

- (a) The use of a high phase-volume ratio (concentrated emulsion).
- (b) A decrease in the particle size of the droplets.

Regarding particle size, emulsions are rather coarse with particle sizes from 5-10 micron, therefore, less stable. To produce a finer emulsion, we

aim at an average droplet size in the neighbourhood of one micron. Naturally, coarse emulsions are less opaque than fine emulsions. Opacity in colloidal dispersions with particle sizes between 0.1 microns and one millimicron is not observed. It can be seen that opacity depends upon particle size and that maximum opacity occurs within a certain range of fine particles.

OPACITY AND COSMETIC PRACTICE

Water in oil emulsions are at present popular in cosmetic practice, especially those prepared from absorption bases. These absorption bases consist essentially of 7-10 per cent woolwax alcohols and woolwax esters dissolved in paraffin hydrocarbons (mixtures of liquid soft and hard paraffins). The internal phase of a W/O all-purpose cream consists of 50-55 per cent of water or of about 50 per cent water and 5 per cent glycerin. In this way, the correct phase-volume ratio is ensured. The chief characteristic of W/O emulsions prepared from lanolin wax alcohols is that they develop coarse primary emulsions. The process of emulsification usually consists of two separate operations. The initial coarse primary emulsion can be produced by relatively simple stirring. The resulting emulsion will be lacking in both opacity and stability. In this operation it is necessary to overcome powerful forces of interfacial tension, forces which oppose adequate dispersion of one phase in the other. Although the presence of the emulsifier reduces the tension, a second step is still necessary. Interfacial tension has still to be reduced to a minimum and a protective film must be formed around the droplets by mechanical means such as violent treatment in a homogeniser or colloid mill. Either of these two machines will produce emulsions of very small particle size of adequate opacity and great stability.

The breaking down of coarse particles into fine globules requires a considerable amount of mechanical energy. The energy required for complete stability will be inversely proportional to the square of the diameter of the particle of the emulsion globules. Homogenisers and colloid mills are designed chiefly for the emulsification of W/O creams. Here the particle size of the globules must be of the smallest so as to ensure lasting stability of the emulsion.

HAND LOTIONS AND HAND CREAMS

Changes in opacity can be established in cosmetic preparations in which the water phase contains a high proportion of glycerin. As previously mentioned, the addition of glycerin increases the refractive index of the aqueous phase. Cosmetic emulsions for the care of the hands usually contain large amounts of glycerin and, therefore, tend to lack opacity. It should be mentioned in passing that some O/W emulsifiers such as glyceryl monostearate, cetyl sulphate, cetyl alcohol, etc., tend to reduce opacity in emul-

sions. To the best of the writer's knowledge, the reason for this behaviour has not yet been explained in the literature.

MOUTHWASH PREPARATIONS

Such preparations contain a moderately dilute alcohol, flavour compound and antiseptics. If we pour a few drops of the mouthwash solution into a beaker, we observe a development of a milky opalescence. The ingredients of the mouthwash are intimately dispersed in the alcohol forming a molecular solution. However, they are insoluble in water. When a few drops of the mouthwash are added to water, the alcohol becomes considerably diluted, and since the flavour oils and preservatives are not soluble in the Water/Alcohol mixture, they appear in the form of exceedingly fine droplets. Without sufficient time to coalesce, they remain dispersed in the water and do not rise to the surface as large droplets. The opalescent fluid can be by no means considered as a true emulsion. Oil hydrosols are highly diluted emulsions of the O/W type with extremely fine particle sizes. The feature which characterises the oil hydrosols is that they do not contain emulsifiers and, in the main, they have little practical value. They are, however, of the highest theoretical interest. The lack of opacity in an oil hydrosol system is obviously in accordance with the previously expressed principles of opacity formation.

FLUID EMULSIONS

The lotion or milk type of cosmetic may be either O/W or W/O liquid emulsions. Normally they contain small amounts of the oil phase. They are sold as hand lotions, facial milks, cleansing lotions, sunburn lotions, etc. Lacking the favourable advantage of high viscosity, they require more care in formulation of manufacture than do the firm creams. Nevertheless, there are, on the market, many lotions of excellent stability and high opacity. This latter property is due to the employment of efficient emulsifiers and homogenisers.

Oils, fats, waxes and other modern hydrophobic materials are used in cosmetics for cleansing, softening, protecting and nourishing human skin. The human skin is basically of a hydrophylic nature and shows little affinity for hydrophobic substances, and it is therefore difficult to introduce these latter materials into the skin. However, in the form of an emulsion, hydrophobic materials are more easy to apply and in addition are more economical in use. In an O/W emulsion the fatty materials are enveloped in the hydrophylic or external phase. This results in good wetting properties and facilitates spreading and penetration into the skin. Despite the distinction between oil and water, they tend to lose their independent properties when in common emulsion. They form an homogeneous system and the dispersion

of oil in water results in a tremendous increase of the interfacial area. One c.c. of a fine emulsion with an average particle size of one micron possesses about one thousand billions of droplets with an interfacial area of 30,000 cm.² or approximately thirty-two square feet. Since the development of opacity is dependent upon particle size, the importance of the above figures can be imagined.

A further advantage of the emulsified system is the possibility of introducing otherwise immiscible hydrophylic and hydrophobic compounds. Cosmetics may contain water-soluble salts, sun screening agents, perfumes and water-insoluble preservatives, etc.

The combination of water in oil cosmetic emulsions brings about a greater degree of cleansing action since the aqueous phase will remove the residues of perspiration and water-soluble dirt, whilst the oil phase will remove fatty excretions of the skin and previously applied cosmetics. One should be aware that certain ingredients, including inorganic salts, might be opposed to the stability of an emulsion. A breakdown in the emulsion system will naturally reduce the opacity. In certain cases a minor instability in the system may lead to reversible changes which are known as sedimentation. Below the upward creaming layer or above the downward creaming layer may appear a partial loss in opacity. The creaming layer itself, however, being the accumulation of emulsified particles, remains fully opaque. A major instability in an emulsion which results in irreversible separation will mean considerable reduction in opacity. This is evident since the breaking of the emulsion has destroyed those optical properties which were in the first place responsible for the opacity. For this reason it is necessary that cosmetic emulsions such as deodorant lotions or creams and sun screen preparations neither sediment nor break.

CONCLUSIONS

Opacity in an emulsion is a function of the refractive indices of the two phases, the ratio of oil and water and the size of the emulsion particles. We have seen that the factors which promote and ensure the stability of emulsions are also responsible for opacity. Opacity may therefore be regarded as a sign of stability and without a doubt lends greatly to the attractive appearance of an emulsion.

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