

GLYCERIN AS A CONSTITUENT OF COSMETICS AND TOILET PREPARATIONS

*An Attempt at Reappraisal by F. V. WELLS**

The characteristic properties are critically discussed and the manner in which these properties contribute to its employment in cosmetics.

GLYCERIN, called by its Swedish discoverer, Carl Wilhelm Scheele, "the sweet principle of fats," is a substance noted above all else for its exceptional physical versatility; a property that is enhanced and accentuated by chemical stability, æsthetic appeal, relatively low cost and a wide range of compatibility with other materials.

I have referred elsewhere to many of the properties and cosmetic applications of glycerin,¹ and an excellent review of the subject has been written by Kalish.² Other papers and articles to which reference may usefully be made in this connection include those of Pickthall,³ Reckless,⁴ Bragg,⁵ Stetson,⁶ and Chadwick and Pears.⁷ An informative review of glycerin as a humectant is to be found in the revised first volume of Harry's work,⁸ and much information of a general character is contained in the broad survey, "Glycerin: its Industrial and Commercial Applications," published in 1945,⁹ and Lawrie's book on glycerin and the glycols.¹⁰

While cosmetic chemists do not need to be told, at this rather late hour of the day, that glycerin is one of their most valuable and versatile raw materials, it is nevertheless opportune, and may prove profitable, I think, to attempt a contemporary reappraisal of its properties and uses. The present survey represents, however imperfectly, such an attempt to consider one by one the several and diverse properties that are uniquely contained in this familiar material, and the ways in which they are utilised in the cosmetic industry.

Probably the most important property of glycerin, so far as the cosmetic chemist is concerned, is its hygroscopicity, or power to absorb and retain moisture. W. C. Griffin and co-workers¹¹ have further defined two aspects of hygroscopicity, namely, *equilibrium hygroscopicity*, which is the state or condition that exists when an aqueous solution of the humectant or hygroscopic agent will neither gain nor lose water at a given humidity (RH), and *dynamic hygroscopicity*, or the relative speed with which a humectant or its aqueous solution will gain or lose moisture while approaching equilibrium. In addition to these two factors, certain other properties must be taken into account when selecting a humectant (or moisture content-stabilising agent) for cosmetic use. It is, for example, desirable that the humectant should be characterised by low volatility, although I do not agree with Griffin

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et al. that complete lack of volatility is necessarily to be preferred. A good cosmetic humectant should, first and foremost, exhibit a high degree of hygroscopicity, and particularly dynamic hygroscopicity, under the normal conditions of use. It should be of low volatility, and cause minimum viscosity changes with variations in temperature and water content. Other desirable features are: lack of toxicity, dermatological suitability, a wide spectrum of compatibility, reasonable cost, and good colour, odour and taste. It is the nicely balanced combination of these and other more general properties that has led such authorities as Kalish to state that "the humectant powers of glycerin are outstanding and account in large measure for its predominant position in cosmetic formulation."

A great deal of useful information is contained in the now well-known paper by Griffin, Behrens and Cross (*loc. cit.*), but in view of the admittedly "erratic" character of some of the recorded weight losses, it would be as well for chemists not to place too much reliance on them. Even ruling out the ever-present possibility of errors in manipulation or measurement, one is faced, in this admirable piece of supplier-sponsored investigation, with (a) data based on cream formulæ that are themselves full of variables and (b) deductions that, while unexceptionable in themselves, do not fully present the story as told by the authors' own tables (i.e., of per cent weight loss in relation to the type and concentration of humectant present). I mention this because it has become almost a fashion to quote these authors' paper as the standard reference to the comparative utility as cosmetic humectants of glycerin, sorbitol and propylene glycol.

Vélon pointed out in 1951¹² the high rate of loss of diethylene glycol from a 75 per cent aqueous solution when dried in an oven at 105° C. and examined at intervals of 3, 5, 11, 16, 20, 28 and 36 hours. After the lapse of 36 hours all the diethylene glycol had evaporated. The loss of glycerin, exposed to similar conditions, was also high, but it was nevertheless much more gradual—ranging gradually from 25 per cent after 3 hours to a maximum of 42 per cent after 36 hours. It may be argued with good reason, however, as with so much published data concerning humectants, that this type of experiment bears little relationship to humectant performance in face creams, where the hygroscopic agent is unlikely to be exposed to the air for long periods or to very high temperatures, and is usually present in proportions not exceeding 10 per cent of the total formula. Also, as Harry truly observes,¹³ "the majority of cosmetic and toilet products are packed in air-tight containers, and the humidity inside the container is then purely a function of the temperature to which the container is subjected."

In the tabulated results of their numerous experiments, Griffin *et al.* state that a soap-type cream containing 10 per cent of glycerin showed a loss of 0.24 per cent by weight after 1 hour at R.H. 50 per cent as compared with 0.55 per cent loss shown by sorbitol and 0.48 per cent by propylene

glycol in comparable experiments. In a non-ionic cream 2 per cent of glycerin showed a loss of 0.40 per cent after 1 hour at R.H. 70 per cent as compared with 0.55 per cent loss with sorbitol and 0.72 with propylene glycol. After 24 hours at R.H. 70 per cent the non-ionic cream containing glycerin had lost only 5.34 per cent of its weight, as compared with 6.04 per cent for the comparable sorbitol-containing cream. I do not quote these results in support of any claims that can be made for glycerin as the cosmetic humectant of choice, but merely by way of comment upon the rather misleading generalisations put forward on pages 17 and 29 of the paper under reference.¹¹

A further important aspect of humectancy that has not so far been touched upon is the humectant action of the film of cosmetic deposited on the skin. Glycerin has long been utilised in pharmacy, medicine and cosmetics for this purpose. The osmotic action of glycerin and dried magnesium sulphate is utilised, for example, in Morison's paste to withdraw water from boils and carbuncles. Glycerin is similarly used in cataplasma kaolini, where it also helps to prevent the poultice from drying out during storage. The traditional softening "emollient" action on the skin of diluted glycerin, as in glycerin and rosewater and glycerin-containing lotions and o/w creams generally, is, of course, largely due to humectancy. Some later published work of Irvin H. Blank¹⁴ relates to the prevention or relief of dry skin conditions by the application of glycerin solutions, designed to "help attract water to the stratum corneum from the environment."

The subject of humectancy cannot be left, however, without at least a passing reference to the fact that this property can sometimes prove undesirable in cosmetic practice if utilised to excess. Excessive concentrations can prove too searching to the skin. The concentrated material is rather unpleasantly sticky, though not so markedly so as sorbitol syrup. Excessive use of glycerin in creams and lotions may cause what Florence Wall¹⁵ aptly calls "polka dot" spottiness in face powder or make-up films subsequently applied over it. Finally, it must be conceded that glycerin is not always to be preferred to the other humectants. In certain formulæ the use of sorbitol, propylene glycol or even hexylene glycol may, for one reason or another, prove more satisfactory. Thus I have used hexylene glycol in a liquid hand cleaner as a combined humectant and solvent. Bandelin and Tuschhoff have recommended the use of a mixture of glycerin and sorbitol as the most effective means of minimising evaporation losses in ascorbic acid syrups during storage. Many more examples of this kind will come to mind.

Another important property of glycerin, from the cosmetic point of view, is its versatile behaviour as a solvent, coupling agent and vehicle. It is almost certainly the most cosmetically useful of water-miscible substances, being miscible in all proportions with both water and ethyl alcohol. It has limited solubility in ketones and esters. The miscibility of aliphatic and

aromatic compounds with glycerin increases with the number of hydroxyl and amine groups, decreasing with the introduction of alkyl groups. Glycerin's insolubility in oils further adds to its value, especially in the formulation of two-layer fluids and, on a much wider scale, in that of emulsions. Many cosmetic and pharmaceutical materials have greater solubility in glycerin than in water or alcohol.¹⁶ In general, however, glycerin is inferior to propylene glycol both as a solvent and an inhibitor of mould growth.

The solubility characteristics of such three-component systems as glycerin-phenol-water, glycerin-alcohol-water and glycerin-benzene-alcohol have been determined as a result of glycerin's long history of industrial utilisation, and the existence of such data somewhat simplifies laboratory assessment of the potentialities of glycerin as a co-solvent. Glycerin is, in fact, frequently included in physical chemistry studies of ternary systems—whether in relation to mutual solubility or to miscibility, density contraction, homogenising action, selectivity or co-solvency. Glycerin acts, by the way, as the conventional "third party" in lubricating greases, where it tends to form, with traces of water, stable gels of improved consistency. Many inter-related explanations have been put forward for this phenomenon, some writers concentrating on the increased solubilisation of soap in hydrocarbons, while others refer to the co-ordinating capacity of glycerin's hydroxyl groups or glycerin's capacity for lowering the temperature of phase transformations.¹⁷ We here approach the territory of transparent soap manufacture and the broad study of soap phases and their behaviour.

One of the most striking features of glycerin is the sharp decline shown in the viscosity of its aqueous solutions. At 20° C. the viscosity of 100 per cent glycerin is 1410 centipoises. At 70 per cent concentration this drops to 22.5 c.p., at 50 per cent to 6 c.p. and at 10 per cent to 1.3 c.p. This property is used to advantage in the formulation of various skin lotions, where a clear, free-flowing liquid is required that has a pleasantly smooth, emollient effect on the skin, is free from stickiness, and has just enough "body" to prevent its being taken for mere coloured water. The relatively low surface tension of glycerin also plays some part in the behaviour of this type of cosmetic.

While still on the subject of viscosity, we may note that the effect of this polyol on viscosity is not always in proportion to the amount added or to its viscosity in the pure state. Cosmetic formulæ contain so many variables that nobody can at present predict, with any great degree of confidence, the exact effect that glycerin will have on the viscosity or stability of any particular emulsion. Sometimes maximum "body" may be achieved with a low proportion of glycerin and decrease upon further addition. In some emulsions (*vide* Kalish) substantial amounts of glycerin are compatible with the maintenance of a desired and reasonably high viscosity; while in others (*vide* de Navarre¹⁸) the presence of smaller amounts of glycerin ensure

fluidity whereas replacement of glycerin with other humectants gives unpourable emulsions. In certain systems glycerin can markedly promote viscosity, either as so-called "local viscosity" or, in the more usual way, by forming highly viscous aqueous dispersions with very small amounts of gums and gum-like polymers.

Segur and Miner, in their studies on a series of vanishing creams,¹⁸ showed how choice of polyol may influence the consistency of such creams. With glycerin, the maximum stiffness was obtained at 7.5 per cent concentration, whereas with sorbitol syrup this maximum effect necessitated the use of 15 per cent.

I am currently making comparisons of the effect on the viscosity of certain simple emulsions of varying proportions of glycerin, sorbitol and propylene glycol, and hope to publish my conclusions at a later date. Meanwhile, I recommend readers to study the interesting observations on humectants in hand creams by S. J. Strianse.²³

The plasticising action of glycerin is made use of in such products as solid cologne sticks (not more than about 5 per cent), deodorant sticks, wave sets and lacquers (to plasticise the residual film left on the hair), and in many other cosmetics that are designed to leave a thin, smooth film on the skin. Closely related to this property of conferring plasticity is glycerin's lubricant, softening and spreading action.

In a typical face cream, glycerin may first of all act as an aid to emulsification and as a promoter of emulsion stability. (This is particularly the case in *o/w* emulsions based on the polyoxyethylene alkyl ethers.) Secondly, it will assist in the maintenance of viscosity at a desired level. Thirdly, it will function as a humectant, preventing the cream from drying out and promoting the maintenance of consistency. On application to the skin, it will enable the film to spread easily, exerting in the process a combined lubricant and plasticising action, preventing "drag" or "balling up." Fifthly, it may soften the skin or (in the case of nasal creams and jellies) the mucous surface to which it is applied. Sixthly, when the emulsion breaks down or tends to become inverted, glycerin facilitates the phase change and keeps the resulting film even, homogeneous and plastic. Finally, it is perfectly stable in these conditions of use, as well as being non-sticky, emollient and pleasant to the touch. What other cosmetic material can boast of such remarkable versatility?

I cannot conclude this brief review without referring to the special utility of glycerin in aerosol formulations. As long ago as 1939, glycerin had been acclaimed as the ideal agent in shaving creams "for keeping the cream mobile and the lather in a moist state when applied."¹⁹ More recently, a noted worker at the Illinois Institute of Technology²⁰ has pointed out that glycerin is often put to work in studies on fluid foams and anti-fogging agents, and is especially valuable in the preparation of dynamically stable

foams. These two uses are considered together by Pickthall⁸ in one of his recent authoritative essays on aerosol formulation. Drawing attention to the general utility of this trihydric alcohol in aerosol-packaged products, he adds that it is in emulsified foam-type products that glycerin really comes into its own. "The most important single factor," he states, in the development of adequate spreading power, body and foam stability "is glycerin." He goes on to quote a formula for a shaving cream containing 20 per cent of glycerin.

Much more could be written on this subject. In tooth pastes and mouth washes glycerin finds application as a sweetening agent, humectant and "throat-conditioner." As Pepper observes,²¹ it has a subsidiary advantage in vanishing creams intended for sale to very cold countries, in that its freezing point-lowering property prevents emulsion breakdown at low temperatures. Glycerin also reduces the stickiness of gum mucilage and gelatinous films (a property that, with its lubricating action, is used to special advantage in jellies for cosmetic, pharmaceutical and gynæcological use).

From the dermatological point of view, little need be said, having regard to this material's known lack of toxicity and freedom from any tendency to provoke harmful skin reactions under normal conditions of use. There is ample evidence in favour of this view and little but vague and unsubstantiated rumours against it. This does not mean to imply that glycerin should be used quite indiscriminately or without intelligent appreciation of all the concomitant factors involved.¹ Significant, perhaps, among recently published work is that of H. Chino,²² who, in biochemical studies of the *Bombyx* silkworm, has revealed for the first time the presence in animal tissues of both glycerol and sorbitol as normal products of metabolism. Also noteworthy is the use of glycerin in the preservation of corneal grafts and bull's semen.²⁴

By way of conclusion, I would like once again to second E. G. McDonough's plea for further fundamental work on the physical chemistry of glycerin. This would be of great value, he pointed out to American glycerin producers in 1954, in determining whether many of its interesting, yet varied, properties could be integrated and explained more simply. "For example (he added) is the strong hydrogen bonding property of glycerin a basis and an explanation for such terms now used as the hygroscopic nature of glycerin, the humectant character of glycerin, the strong solvent action of glycerin, the high viscosity of glycerin, and the plasticising action of glycerin on such widely divergent materials as proteins (e.g., gelatin, casein, zein and gluten), methyl and carboxymethyl celluloses, amylose and starches, polyvinyl alcohols, alginates and pectates?"

The subject is important enough to deserve the lucid and elegant interpretation of an A. E. Alexander or the subtle analysis of a Linus Pauling.

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SELECTED PHYSICAL PROPERTIES OF GLYCEROL-WATER SOLUTIONS

Glycerol % wt.	Boiling Point ° C. at 760 mm.	Specific Gravity 20/20° C.	Viscosity Centipoises 20° C.	Freezing Point ° C.	Per Cent Relative Humidity at Equilibrium.
100	290	1.26362	1410	18.0	0
99	239	1.26105	1150	15.9	4
98	208	1.25845	939	13.9	9
95	164	1.25075	523	7.7	20
90	138	1.23755	219	1.6	32
70	114	1.18355	22.5	38.9	65
66.7*	112	1.17448	17.5	46.5	67
50	106.7	1.12845	6.00	23.0	82
30	102.9	1.07470	2.50	9.5	92
10	100.7	1.02395	1.31	1.6	98
0	100.0	1.00000	1.005	0.0	100

* Eutectic mixture, minimum freezing point. (Table reproduced from "Glycerine: Properties and Uses," issued by the Glycerine Producers' Association, U.S.A.)