

THE STABILITY OF OILY CREAM B.P.

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Oxidation of Wool Alcohols B.P. in stored Oily Cream B.P. is insignificant and does not affect the stability of the cream, but the method of preparation, and the amount of autoxidation in the wool alcohols used in making the cream, do affect stability. Storage of wool alcohols before use, as a mixture with Liquid Paraffin B.P. or Liquid Lanolin "60" (a solvent segregation product of Anhydrous Lanolin) greatly reduces autoxidation. Liquid Lanolin "60" also acts as an auxiliary emulsifier and imparts stability. Modifications to the official method of preparation are suggested.

OILY Cream B.P. formerly known as Hydrous Ointment B.P. is known sometimes to separate during storage. Muirhead and others¹ found that the breakdown was caused by oxidation of wool alcohols in the cream. Insolubility of the alcohols in the paraffins also present ensued, and thus the amount of active emulsifying agent was reduced.

Muirhead and others¹ found the oxidation of the wool alcohols to be rapid in an emulsion similar to this cream, as shown by changes in acid value. Since the rate of oxidation far exceeded that encountered by the present authors, it was decided to investigate the subject further.

The present work is concerned with distinguishing between the oxidation of wool alcohols in the cream, and their autoxidation during storage before use. It is also concerned with minimising autoxidation without resorting to antioxidants, and improving the stability of the cream with an auxiliary emulsifying agent and by modifying the official method of preparation.

Since Oily Cream B.P. contains a high proportion of liquid paraffin, the effect on autoxidation of storing wool alcohols, before use, as a mixture with liquid paraffin, has been studied, as softening wool alcohols in this manner avoids brittleness and the formation of small pieces which if they remain in storage may oxidise extensively as a result of their having relatively large surface areas.

Because the emulsifying system of the cream was not considered to be satisfactory, and easily affected by oxidation or unsuitable technique of preparation, the effect of adding an auxiliary emulsifying agent has been examined. A liquid was chosen because it could also replace liquid paraffin for eliminating brittleness during storage. The auxiliary emulsifier was a solvent segregation product* of anhydrous lanolin derived from the same parent substance as wool alcohols, and is completely miscible with it as well as with the other ingredients of the cream. Mixtures of it with wool alcohols yield emulsions of greater stability than those given by either substance alone. Also it is chemically similar to anhydrous lanolin, and is equally acceptable or beneficial dermatologically.

* Liquid Lanolin "60", supplied by Westbrook Lanolin Company.

EXPERIMENTAL AND RESULTS (I)

The work was in two stages, the first consisting of 4-month storage tests at room temperature on anhydrous wool alcohols† and blends of this with both liquid paraffin and Liquid Lanolin "60", in good and bad storage conditions. The second stage was storage and stability tests on Oily Cream prepared from each of the 4-month old samples.

The tests were made with the following systems.

(i) Wool alcohols filled whilst molten into a 1-kg. lever-lid tin to leave the minimum air-space. The lid was hermetically sealed with adhesive tape.

(ii) Wool alcohols scraped into thin shavings, spread in a shallow layer on a tray and loosely covered with a sheet of paper.

(iii) A mixture of the wool alcohols with Liquid Paraffin B.P. in the ratio 1:2 by weight, hermetically sealed into a tin as in (i).

(iv) A mixture similar to that of (iii) but as a layer $\frac{3}{4}$ in. (19 mm.) deep in a 56 lb. (25 kg.) anti-corrosive-coated steel drum, the lid being loosely fitted.

(v) A mixture of the wool alcohols with Liquid Lanolin "60" in the ratio 1:2 by weight, hermetically sealed in a tin as in (i).

(vi) A mixture similar to (v) filled into a drum as in (iv).

The acid values of all six systems were determined at the beginning of the storage period, and at the end were re-determined both on the upper $\frac{1}{8}$ in. (3 mm.) of the sample and on the total sample after melting and mixing. (A test on the surface of the flaked wool alcohols was not feasible.) The results are listed in Table I.

TABLE I

INCREASE IN ACIDITY OF ANHYDROUS CREAM BASES AFTER 4 MONTHS STORAGE

System	Acid value		
	Original	After storage	
		Surface	Mixed
(i) Wool alcohols	1.14	1.56	1.22
(ii) Wool alcohols, flaked	1.14	—	12.20
(iii) Wool alcohols + liquid paraffin	0.38	0.44	0.38
(iv) " " "	0.38	0.48	0.42
(v) Wool alcohols + Liquid Lanolin "60"	1.42	1.58	1.44
(vi) " " "	1.42	6.64	1.94

DISCUSSION (I)

(i) Autoxidation of the surface of the wool alcohols stored under good conditions for 4 months is appreciable, although the final acidity is well within the B.P. limit. The acid value of the mixed sample indicates the main bulk to have been unaffected.

† "Golden Dawn" Wool Alcohols B.P. supplied by Westbrook Lanolin Company.

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(ii) The large increase in acidity under these drastic conditions confirms earlier findings²⁻⁴, as does the fall in cholesterol content of the sample from 36 to 16 per cent.

(iii) and (iv) The blending with liquid paraffin had a pronounced inhibiting action on autoxidation of the wool alcohols. Even under the severe conditions prevailing in system (iv) the oxidation was less than that of the pure wool alcohols hermetically sealed in a tin. Under good conditions (system iii), no increase in acid value could be detected in the melted and mixed sample.

(v) The rise in acidity here also is less than that of the pure wool alcohols, notwithstanding that Liquid Lanolin "60" and similar products, like their parent substance anhydrous lanolin, are liable to autoxidation, although to a lesser degree than wool alcohols.

(vi) Under these severe conditions autoxidation of either the Liquid Lanolin "60" or the wool alcohols, or both, is much increased on the surface. The acidity of the mixed sample, however, showed the affected surface to have been less than 2 mm. deep.

EXPERIMENTAL (II)

Storage of Oily Cream Samples

A batch of 400 g. of Oily Cream B.P. 1958 was prepared from each of the samples used in the storage tests described. This formula differs from that used by Muirhead and others, but we preferred to base our work on the official preparation.

Since the method of preparation can affect the stability of the cream, the details are given here.

All components of the oil phase were melted together and adjusted to 50° in the bowl of an electric food mixer fitted with twin beaters. With the mixer operating at full speed the water, at room temperature, was added gradually, mixing continuing for 2 minutes. In addition, the bowl was rotated by hand and the mixing assisted by guiding the emulsion into the beaters with a spatula. The emulsion, cooled to room temperature, was given a final full-speed mix for 2 minutes.

The creams so prepared were packed into glass-stoppered, clear glass jars of 250 g. capacity. One jar of each cream was stored at 38° for 5 months, a second jar of each being kept at room temperature protected from direct sunlight for the same period, after which each cream was examined. A portion of the oil phase from the incubated creams stored at 38° was used for the determination of acid value, using the method of Muirhead and others.

RESULTS (II)

Examination of Creams Stored at Room Temperature

Consistency. This was assessed by "feel", using a spatula. System (ii) produced the softest cream, the other five preparations being similar to each other.

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The acid value of the oil phase containing the flaked wool alcohols was lower than the initial value. This may be due partly to the fact that a proportion of these highly oxidised alcohols was insoluble in the paraffins (as a result of oxidation) and a part was not incorporated in the cream, but adhered tenaciously to the mixer blades. The insoluble portion had a much higher acid value than the remainder, and the loss in the mixer could account for a lowering of the acid value. Another possible reason is that polymerisation or inter-esterification of the free fatty acids in the oxidised wool alcohols occurred during storage of the cream, and that the rate of this polymerisation was greater than the production of new acids by oxidation. Such polymerisation or inter-esterification is associated with the autoxidation of wool alcohols.

The outstanding aspect of the results is their difference from those of Muirhead and others, in particular the relatively small increases found by us in acidity of the oil phases. These authors also found that the separation of their emulsions occurred in as little as 26 hours. This may be accounted for by the different formula used, which contained as much as 68 per cent of water and only 2 per cent of wool alcohols. This formula might be considered too unstable for reliable comparisons were it not for the effectiveness of the 0.007 per cent of Progallin in preventing breakdown. Also this difference would not account for the rapid rise in acid value that they observed. Unfortunately they gave no details of preparation. Even if abnormal amounts of entrapped air were present, the rates of increase in acidity were far beyond our experience.

This point was investigated further. Four batches of emulsion were prepared to the formula of Muirhead and others. Although they quote a viscosity of 74 Redwood seconds for their white oil, no temperature is specified. The oil we used had a viscosity of 121 seconds at 38°, this being the thinnest oil obtainable. The emulsions were made with our technique from four different lots of wool alcohols, representing three different manufacturers. Antioxidants were incorporated in two further emulsions, and all were stored in half-full cans at 38°. Acid values of the oil phase were determined at the start, and again after 48 hours. The results in Table III are calculated on the wool alcohol content only, the paraffins having an insignificant original acid value.

TABLE III
CHANGES IN ACID VALUE OF OIL PHASE AT 38°

Wood alcohols Reference	Acid value	
	Initial	After 48 hours
A	1.98	2.43
B	1.74	1.84
C	0.27	0.30
D	0.90	0.90
B + 0.007 per cent P.G.*	1.85	1.84
B + 0.05 per cent B.H.A.†	1.90	2.00

* Propyl gallate. † Butylated hydroxyanisole.

The emulsions showed a varied separation, but none separated completely, and the antioxidants did not appear to have a significant effect upon stability.

The increases in acidity were much less than those found by Muirhead and others, even though storage at 38° was over a longer period. The reason for this difference remains obscure, but the wool alcohols they used must have been exceptionally susceptible to oxidation. Also there has been an improvement in the quality of pharmaceutical wool alcohols since their paper appeared.

The inferences that may be drawn from our results are that oxidation of Wool Alcohols B.P. 1958 whilst in Oily Cream B.P. is insignificant and has little if any effect upon stability, but the oxidation which may occur in wool alcohols before being incorporated in the cream can have a deleterious effect and must be avoided. Storage of the alcohols as a mixture with liquid paraffin or with a solvent segregation product of anhydrous lanolin, such as Liquid Lanolin "60", reduces autoxidation. The latter provides the additional advantage of increasing the basic stability of the Oily Cream without altering its consistency.

Technique of Preparation of Oily Cream

The B.P. 1958 specifies no temperatures to be observed when preparing the cream, only that the water should be added to the melted fats with constant stirring, followed by mixing vigorously until a smooth cream is obtained and stirring until cold.

A batch of the cream was so prepared, melting the fats to 80° and adding the water at room temperature, with constant stirring. The emulsion was transferred to an electric mixer and vigorously mixed for 2 minutes, after which it was stirred at intervals by hand until cold.

From similar ingredients the cream was also prepared by our technique, but in addition was passed through a piston-type homogeniser.

The two creams were stored at room temperature for 4 weeks, when the B.P. preparation was found by the microscope slide test to contain appreciably more free water and also to have a distinctly coarser emulsion structure than the cream prepared by our method.

Therefore a more detailed specification of the method of preparation seems necessary, and a modification on the lines we have described would be beneficial to the stability of Oily Cream.

REFERENCES

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4. Horn, *J. Sci. Food Agric.*, 1958, **9**, 632.