THE RESISTANCE OF ACETYLATED LANOLIN DERIVATIVES TO HYDROLYSIS

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A study was made of the stability of acetylated lanolin derivatives *per se* and in anionic emulsions. The stability of the products was expressed in terms of % hydrolyzed material, while the stability of the emulsions was expressed as changes of pH. A comparison was made with stability tests on emulsions containing acetylated monoglycerides.

THE OBJECT of this paper is to report on studies of the resistance of acetylated lanolin derivatives to hydrolysis. This investigation was initiated some three years ago when the growing importance of these products as cosmetic and pharmaceutical ingredients necessitated detailed data on the subject. It was apparent from initial evaluation work that the acetates of lanolin, lanolin alcohols and lanolin alcohol ricinoleate evinced many of the stability characteristics of waxes.

Lanolin is a wax composed mainly of esters of higher aliphatic and polycyclic alcohols. Like all waxes it is glyceride-free. It is fairly resistant to hydrolysis and to saponification by methods effective on glyceride fats. Truter[1] presents a detailed description of this interesting subject. Experienced cosmetic formulators are familiar with the characteristics of lanolin and it is hoped that this presentation will supply information on the stability of acetylated lanolin derivatives important for their practical application to cosmetic emulsions.

STABILITY OF ACETYLATED PRODUCTS

EXPERIMENTAL

The following acetylated lanolin derivatives were used in this experiment :

Acetylated lanolin

Acetylated lanolin alcohols

Acetylated ricinoleate of lanolin alcohols

Retained room temperature shelf samples of plant production batches of the above materials were analyzed periodically for percent water soluble

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acids and percent free fatty acids. An increase in water soluble acids would indicate the hydrolysis of the acetate. An increase in free fatty acids would include water insoluble acids resulting from either hydrolysis of lanolin esters or oxidation. Percent water soluble acids was determined by the following method :

50 g of material were dissolved in 150 cc of benzol, placed in a separatory funnel and extracted three times with 25 cc hot water each time. The combined aqueous extracts were titrated with 0·1 N methanolic KOH using phenolphthalein as indicator. The titration result was first calculated as percent acetic acid and then converted to percent hydrolyzed material by the following formula:

Calculation of % Hydrolyzed material

$$\frac{\text{Equiv. wt. Acetic Acid}}{\text{Equiv. wt. Acetylated Prod.(calc.)}} \times 100 = \%\ \text{Sol. Acids on Compl. Hydrolysis}$$

For Acetylated Lanolin $\frac{60}{2060} \times 100 = 2.91\%$ " " " " "

For Acetylated Lanolin Alc. $\frac{60}{320} \times 100 = 18.7\%$ " " " " "

For Acet. Lan. Alc. Ricin. $\frac{60}{650} \times 100 = 9.2\%$ " " " " "

$$\frac{\%\ \text{Soluble Acids found on Aging (determined)}}{\%\ \text{Soluble Acids on complete hydrolysis (calc.)}} \times 100 = \%\ \text{Hydrolyzed material}$$

Results

The data on percent hydrolyzed material as determined by this method are expressed in *Figure 1*.

It will be noted that percent hydrolyzed material is very low for all three products. Even the highest of these, acetylated lanolin, contained only 0·4% hydrolyzed material after ageing 36 months. This represents an insignificant increase and it therefore can be concluded that these three materials have exhibited excellent stability at room temperature during the three-year observation period.

Although it was felt that the soluble acids expressed in *Figure 1* as

percent hydrolyzed material is the most significant measure of the hydrolysis of the acetate, it was also deemed interesting to follow the changes in free fatty acid content on ageing. The increase in percent free fatty acid determined on retained shelf samples of the three derivatives over a period of approximately three years is depicted in *Figure 2.* A sample of cosmetic grade lanolin USP was included in the study for comparison of rates of free fatty acid development.

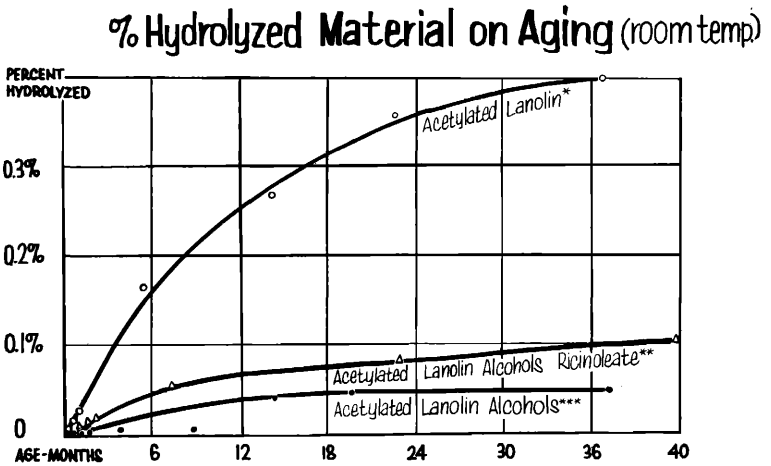

Figure 1

The curves portray the increase in percent free fatty acid above the level found in the freshly manufactured sample. It is obvious from the flat low-level curves, that the development of FFA in the acetylated products is again extremely low. The FFA increase in lanolin on ageing is steep in the sample studied. This is known to occur and had been reported previously by several investigators[2, 3]. The lanolin sample increased 3% in FFA whereas the acetylated derivatives went up no higher than 0·25% in 3 years.

It is interesting to comment on a possible reason for this unexpected stability after acetylation. The free fatty acid increase in lanolin occurs at the expense of the alcohols and as a result of the oxidation of the latter. N. W. Gillam established this in 1947.[2] Kitchen and Clark[3] reported that auto-oxidation takes place in the top layer of woolfat when stored for 12 months in an open container, the changes manifesting themselves in an increased acid number and peroxide value, decreased cholesterol content and rancid odour. They also established that these changes can be accel-

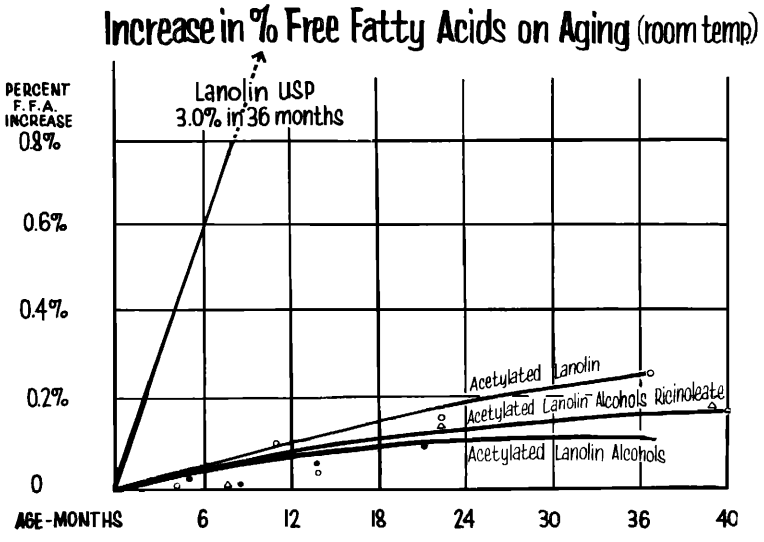

Figure 2

erated, and perhaps even initiated by traces of metal, especially by traces of manganese and copper.

The processing steps involved in manufacturing and purifying acetylated lanolin derivatives decrease the ash content, including trace metals, by as much as 90% and also remove oxidized impurities. This purification, in the light of the work cited above, might well account for the greatly improved stability of the acetylated products.

The decreased sensitivity to acetylated lanolin derivatives on the part of lanolin sensitive persons which has been reported by several investigators[1, 4, 5] might also be a reflection of the removal of, or decrease in formation of, oxidation products.

All samples were checked periodically for changes in colour and odour. In the case of the two liquid products, acetylated lanolin alcohols and acetylated ricinoleate of lanolin alcohols, clarity was also checked. No changes were observed over the period of these studies in any case except in lanolin where a strong odour developed.

Stability of Acetylated Products in Emulsions

Although it is important to know the effect of ageing on the acetylated lanolin products *per se*, it is of greater practical value to learn how resistant to hydrolysis they are under conditions of actual use in emulsion formulas. Soap systems were selected for this study because of their wide application

and because their alkalinity could favour hydrolysis. Progress of hydrolysis was followed by pH measurements. An initial experiment was carried out on a typical anionic germicidal lotion containing acetylated lanolin alcohols. The formula for this emulsion and its control which contained mineral oil instead of acetylated lanolin alcohols is as follows :

	Test Emulsion	*Control Emulsion*
Mineral Oil, 70 vis.	10·0%	14·0%
Acetylated lanolin alcohols	4·0	—
Stearic Acid XXX	4·5	4·5
Hexachlorophene	0·25	0·25
Glycerine..	5·0	5·0
Triethanolamine	1·0	1·0
Water, distilled	75·25	75·25
Preservative	q.s.	q.s.

Samples of these emulsions in two ounce lotion bottles were stored both at room temperature and in the incubator at 42°C. They were removed periodically from storage, shaken, and pH measurements made at 25°C using the Beckman pH Meter, Model H–2. The pH readings were as follows :

	Test Emulsion pH		*Control Emulsion pH*	
	Room	Inc.	Room	Inc.
Initial	8·4	—	8·1	—
2 weeks	8·4	—	8·1	—
2 months	8·3	8·2	8·0	7·7
3 months	8·2	7·9	8·0	7·9
4 months	8·2	7·9	8·0	7·8
5 months	8·1	7·8	7·9	7·7
7 months	8·0	7·7	7·9	7·6
8 months	8·1	7·7	7·9	7·5
Total change after 8 months ..	0·3	0·7	0·2	0·6
*Change attributable to Acet. Lan. Alcs.	0·1	0·1	—	—

The data reveal that small changes in pH occurred during the eight-months' study. The test emulsion dropped 0·3 pH at room temperature and 0·7 pH in the incubator. The control emulsion dropped almost the same amount ; 0·2 pH at room temperature and 0·6 in the incubator. The change attributable to acetylated lanolin alcohols in each case was the difference between the control and the test emulsions. This amounted to 0·1 pH over a period of eight months which is obviously within the error of the instrument. Although no particular attempts had been made to formulate for stability, the emulsions exhibited good shelf life over the period of the test. The incubator samples showed some sign of separation after seven months while the room samples remained perfectly stable. No odour was evolved throughout the eight months' period of the study.

After the above experiment was completed, a second series of emulsions

was prepared to compare the stability of four different oil soluble acetylated derivatives in an oil-in-water system at both room and incubator temperature (42°C). pH changes were again used as a measure of hydrolysis of acetate.

Experimental

The following were used in this experiment:

Acetylated lanolin
Acetylated lanolin alcohols
Acetylated ricinoleate of lanolin alcohols
Acetylated monoglycerides [distilled acetylated monoglycerides (from lard)]

The last product, although not a lanolin derivative, was included in this study in order to compare the stability of this material with that of the acetylated lanolin derivatives. The emulsion formula varies slightly from the one used in the preliminary study. A control was used in which mineral oil was substituted for the acetylated products. The formulae are as follows:

	Test Emulsion	*Control Emulsions*
Acetylated Derivative	4·0	— —
Mineral Oil (70 vis.)	10·0	14·0
Stearic Acid XXX	4·5	4·5
Triethanolamine	1·0	1·0
Glycerine..	5·0	5·0
Distilled Water	75·5	75·5
Preservative	q.s.	q.s.

Results

The pH readings were as follows:

pH of Emulsions on Aging. II

Formula Containing	Room Temperatures						Incubator Temperatures				
	initial	2wks.	4wks.	6wks.	10wks.	corr.* change	2wks.	4wks.	6wks.	10wks.	corr.* change
Control	8.0	7.9	8.0	8.1	8.0	---	7.8	7.8	7.8	7.7	---
Acetylated Lanolin Alcohols	7.9	7.8	7.8	7.8	7.7	0.2	7.6	7.6	7.7	7.4	0.2
Acetylated Lanolin	8.1	7.9	7.8	8.0	7.9	0.2	7.7	7.9	7.9	7.8	0
Acetylated Lanolin Alcohols Ricinoleate	8.1	8.0	7.9	8.0	8.0	0.1	7.9	7.7	7.9	7.8	0
Acetylated Monoglycerides	8.0	7.8	7.8	7.8	7.6	0.4	7.6	7.3	7.1	6.6	1.1

* CORRECTED CHANGE - Change in pH after 10 weeks minus control pH change - room temp. 0, incubator temp 0.3

Only minor changes in pH were evidenced in any of the above emulsions except in the preparation made with acetylated glycerides. Here a corrected change of 0·4 pH at room temperature and 1·1 pH in the incubator were significantly accompanied by the breaking of the emulsions and odour development. The changes in pH in the emulsions made with acetylated lanolin derivatives were in most cases within the range of accuracy of the pH meter. There was no change in stability nor in odour development. We cannot explain the instability of the acetylated monoglycerides in an emulsion system as compared to the acetylated derivatives of lanolin. This may reflect a basic difference between the stability of glyceride fats and non-glyceride waxes.

Discussion

It was anticipated from previous experience that some drop in pH would occur on the ageing of soap emulsions of the type studied. The control emulsions did demonstrate a pH drop and this had to be subtracted from that of the test emulsions in determining pH change attributable to hydrolyzed acetate.

A possible explanation for this pH drop in the control emulsions may be the tendency toward the formation of "acid soaps" attributable to the association of stearate soaps with free stearic acid. Such "acid soap" compounds have been reported with pH readings as low as 6·0[6].

It was recognized that pH measurements might not detect a very slight degree of hydrolysis in the test emulsions. However, a significant pH change beyond that of the control was obtained with emulsions containing acetylated monoglycerides. This was associated with a loss of emulsion stability.

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Discussion

Dr. W. W. Myddleton : The authors suggest in the preprint that the stability of the acetylated monoglyceride may be attributed to the presence of preservatives and antioxidants in the sample studies. Were these

additives known to be present and is it the practice of manufacturers of cosmetic materials to make such additions without disclosing the fact ? Is it considered likely that the acetylated monoglycerides might exercise a preservative action like that of triacetin, inhibiting the growth of micro-organisms either in the bulk cosmetic product or as a skin antiseptic ? Might this account for the stability of the acetomonoglyceride *per se* ?

THE LECTURER : I am sorry but I cannot answer for an industry. I can say for our own company, and I think for all those companies in our related business, that they do not generally add any antioxidants or preservatives, but it has been known to happen, and I think you all are familiar with the fact that antioxidants have been added to mineral oil for a long time. At least in the United States—for a long time before it was made public. In this particular sample we did not know whether it was present or not. We just assumed so.

MR. S. COHEN : I would like to add that antioxidants and preservatives are generally not added to saturated monoglycerides. However in the case of liquid or plastic-type emulsifiers having high Iodine Values, antioxidants are useful and are often added to increase stability. In the United States the amount and type used are generally stated. It is suggested that the cosmetic chemist request this information from the supplier if it is important to him.

MR. F. ATKINS : Whatever the reason for the drop in pH value in the formula containing acetylated monoglycerides, it seems to me most improbable that oxidative rancidity is involved, whether that material contained any antioxidant or not. Triethanolamine is one of the most efficient antioxidants we have and the cream formula tested contains more than sufficient to present rancidity development. The "acid soap" formation suggested by the author seems much more probable to me.

MR. H. CARTER : Is it possible that the reason for the stability of the acetylated lanolin derivatives is due to the presence of enzymes analogous to the lipolytic enzymes of fats which are inhibited by acetylation ?

THE LECTURER : It is possible. Although lanolin does not undergo enzymatic cleavage too readily. It does not lend itself too readily to growth of organisms.

DR. B. L. RAO : Are the acetylated lanolin derivatives stable to sunlight ?

THE LECTURER : All shelf samples are stored in the dark. I should have mentioned that.