

## WOOL ALCOHOLS

### PART I—OBSERVATIONS ON CHANGES IN PHYSICAL AND CHEMICAL PROPERTIES IN WOOL ALCOHOLS AS A RESULT OF OXIDATION

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IN view of the increase in the use of wool alcohols\* as an emulsifying agent in the preparation of pharmaceutical creams and ointments, and in particular, the inclusion of monographs on wool alcohols and ointments derived therefrom in the British Pharmacopoeia, it was considered that some results of investigations carried out in these laboratories on various aspects of the chemical and physical behaviour of wool alcohols would be of value to pharmaceutical workers.

A review of the literature indicates that very little information exists concerning the properties of wool alcohols and their behaviour when stored under different conditions. The results presented in this paper refer specifically to one particular grade of wool alcohols available in this country,† although experience gained by us suggests that wool alcohols produced in these and other associated laboratories differ in certain properties. It has been known for some considerable time that certain characteristic changes occur when wool alcohols are stored in air.<sup>1,2</sup> For example, exposure of samples of the material to the atmosphere gives rise to a change in surface characteristics and suggestions have been made in the literature that this change is due to oxidation. Gillam,<sup>3</sup> for example, reports that wool alcohols when exposed to atmospheric conditions, for considerable periods of time, show a marked increase in fatty acids, as denoted by rise in acid value, and it has been noted by us that wool alcohols, when subjected to irradiation with ultra-violet light showed marked changes in physical characteristics and rise in acid value. It has also been observed that these changes are slowed down by the addition of small quantities of antioxidants (e.g., pyrogallol,  $\alpha$ -tocopherol). It has been our experience over several years that samples of wool alcohols when stored in bulk prior to use in a technical process, showed marked rises in acid value and such samples, on examination according to the B.P. monograph, possessed acid values as high as 30, and some samples contained negligible digitonin-precipitable material. It was also noted that such wool alcohols were unsuitable for use in the manufacture of water-in-oil emulsions.

Although we have shown that breakdown of water-in-oil emulsions is due to several factors other than the nature of the emulsifying agent itself (e.g. nature of hydrocarbon used, conditions employed in

\* The term wool alcohols throughout this paper refers to the total unsaponifiable fraction of lanoline and is not necessarily synonymous with Wool Alcohols B.P.

† The wool alcohols used throughout this investigation were obtained from Messrs. Croda Ltd., and are marketed under the trade name "Hartolan."

emulsification), it has been apparent that the initial nature of the wool alcohols or changes which they might have undergone during storage in the emulsion, may adversely affect the stability of the product. For example, a series of comparable emulsions prepared from wool alcohols of different origin showed marked differences in stability and those which tended to separate more readily showed a marked rise in acid value of the isolated oil phase, such rise being retarded by the inclusion of antioxidants.

In view of these observations it was considered that a quantitative study should be made of some of the physical and chemical properties of wool alcohols when treated as follows:—irradiation by means of ultra-violet light, exposure of the solid material to air at normal or elevated temperatures, and treatment of molten material with oxygen. This paper records some of the results obtained and the methods used. The changes in physical and chemical constants were measured by periodic determination of some or all\* of the following:—

1. Surface activity ; 2. Appearance ; 3. Acid value ; 4. Saponification value ; 5. Acetyl value ; 6. Digitonin-precipitable fraction.

#### EXPERIMENTAL

For convenience, the work will be described under the following sub-headings:—1. Treatment of molten wool alcohols with gaseous oxygen ; 2. Exposure of wool alcohols to atmospheric oxygen ; 3. Irradiation of wool alcohols with ultra-violet light ; 4. Examination of wool alcohol emulsions after storage.

1. *Treatment of molten wool alcohols with gaseous oxygen.* The following method and equipment were devised with a view to producing a uniform rate of oxidation and causing appreciable changes in the material within reasonable periods of time. The apparatus is illustrated in Figure 1.

Oxygen enters at A and passes through the aperture B of the hollow glass stirrer G and partially through the stirrer guide C. It enters the molten wool alcohols through the holes D, E & F, in the stirrer and also through the base of the stirrer guide at H. Gas leaves the vessel at the side tube I and its flow rate was measured by a suitable meter. The lower portion of the apparatus was surrounded by a removable steam jacket so that test samples could be withdrawn via J. The stirrer speed was approximately 300 revolutions per minute. Samples for analysis were withdrawn at the intervals quoted and the results obtained are tabulated in Table I. A control experiment was carried out substituting carbon dioxide for oxygen. In this way it was shown that negligible changes of the wool alcohols occurred in the absence of oxygen even on heating for the time quoted. As a further precaution the effluent gases were trapped in a wash bottle cooled with solid carbon dioxide so that any acidic volatile matter produced could be estimated by titration

\* The changes which wool alcohols undergo on treatment with gaseous oxygen have been chosen as typical of those which occur in the other three methods and for convenience the full physical and chemical constants were determined only in Experiment 1.

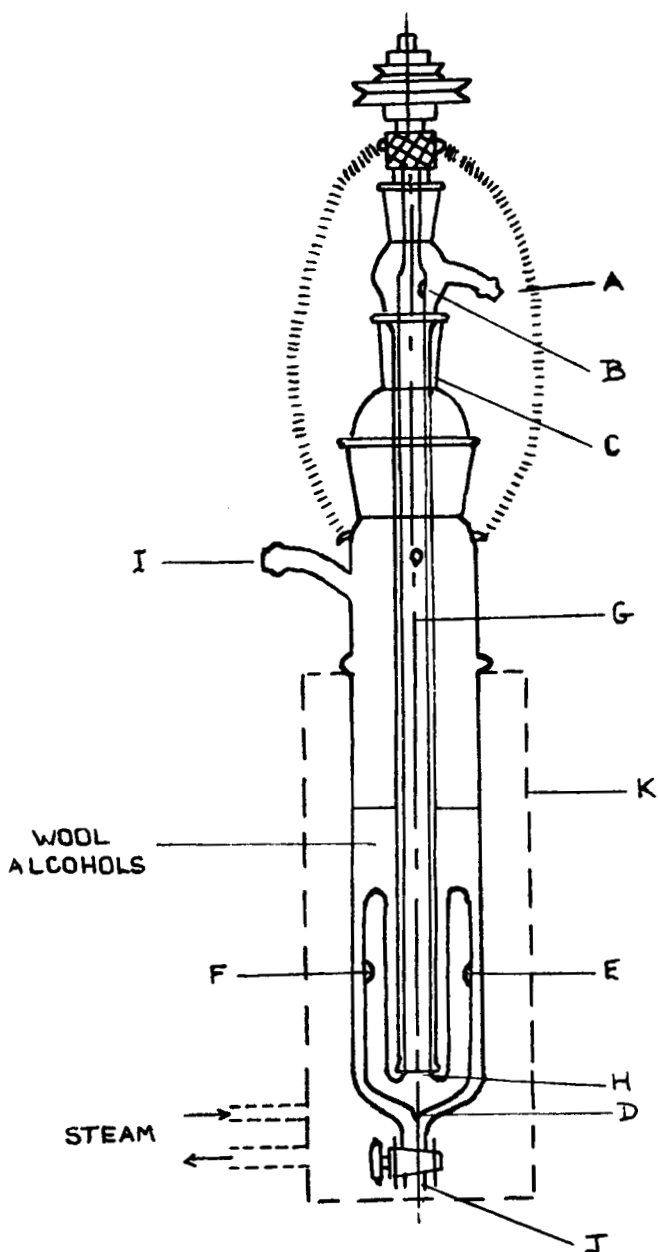


FIG. 1. Apparatus for the treatment of molten wool alcohols with gaseous oxygen in alcoholic solution. A small acidic fraction was obtained in this way which constituted approximately 1 per cent. of the total acidity and this was ignored in the acid values quoted in Table I.

2. Exposure of wool alcohols to atmospheric oxygen. The wool

# WOOL ALCOHOLS. PART I

**TABLE I**  
CHANGES IN CHEMICAL AND PHYSICAL PROPERTIES OF WOOL ALCOHOLS DURING OXIDATION

Time of oxygenation in hours	Acid value	Ester* value	Acetyl value	Cholesterol content (digitonide method) per cent.	Interfacial Tension Dynes/cm. Age of interface	
					60 secs.	120 secs.
0	2.5	4.7	134	30.40	8.5	7.4
5	4.0	23.4	132	25.49	10.6	9.6
10	5.3	24.1	122	23.85	—	9.2
20	8.1	32.5	—	20.43	8.1	7.2
30	12.0	38.6	110	15.14	7.6	6.5
40	16.0	61.2	—	8.32	6.1	4.7
50	25.4	62.0	—	4.99	4.3	3.9
60	31.1	78.6	86	0.81	4.5	3.7
70	34.0	96.0	—	—	5.2	4.5
80	35.3	96.7	55	—	4.3	4.0
90	38.4	96.6	—	—	5.1	4.4

\* Difference between saponification value and acid value.

alcohols were obtained in suitably thin layers by pouring the molten material into large photographic developing dishes to a depth of 1/16 inch. The samples were then exposed to the atmosphere at the normal temperature and in an incubator at 37°C. Samples were withdrawn periodically and their acid values determined. The results are shown graphically in Figure 2.

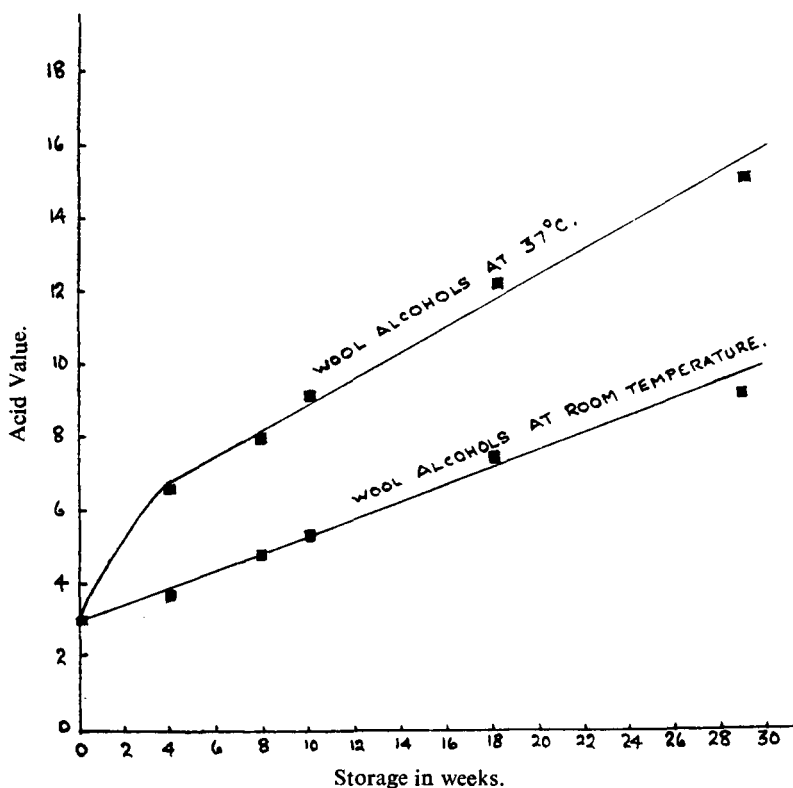


FIG. 2.

3. *Irradiation of wool alcohols with ultra-violet light.* The material was prepared in thin layers as in the previous experiment and exposed to the radiation of an Hanovia ultra-violet lamp, the quartz tube being approximately 8 inches from the surface of the wool alcohols. Samples were withdrawn at intervals and their acid values determined. The experiment was repeated using wool alcohols containing antioxidants. The results are shown graphically in Figure 3.

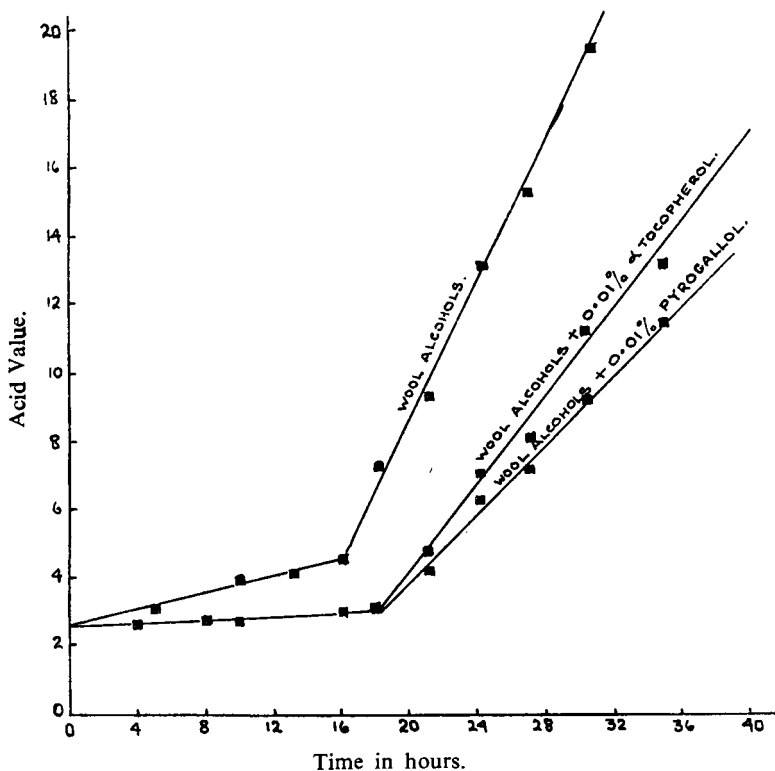


FIG. 3.

4. *Examination of wool alcohol emulsions after storage.* Two emulsions were prepared according to the following formula, one containing 0.007 per cent. w/w of propyl gallate.

Wool Alcohols	...	...	...	...	20
Paraffin wax	...	...	...	...	100
White oil (viscosity 74 Redwood secs.)	...	...	...	...	200
Water	...	...	...	...	680

The samples were packed in lacquered tinsplate containers leaving a considerable air space above the emulsion and stored at room temperature and at 37°C. Samples were observed at various intervals of time, the appearance being noted and the acid value of the total oil phase determined by the following procedure:—A sample was withdrawn and twice its weight of warm water added. It was then heated on a steam bath until the emulsion had separated into distinct clear layers. The

## WOOL ALCOHOLS. PART I

oily layer was then separated and a suitable weight used for the determination of acid value as described later. It was assumed that only wool alcohols were responsible for any change in acid value of the oily phase and the value was calculated with reference to the known wool alcohol content. During the experiment some of the emulsions partially separated but the acid value determinations were nevertheless continued. The results are illustrated in Figure 4.

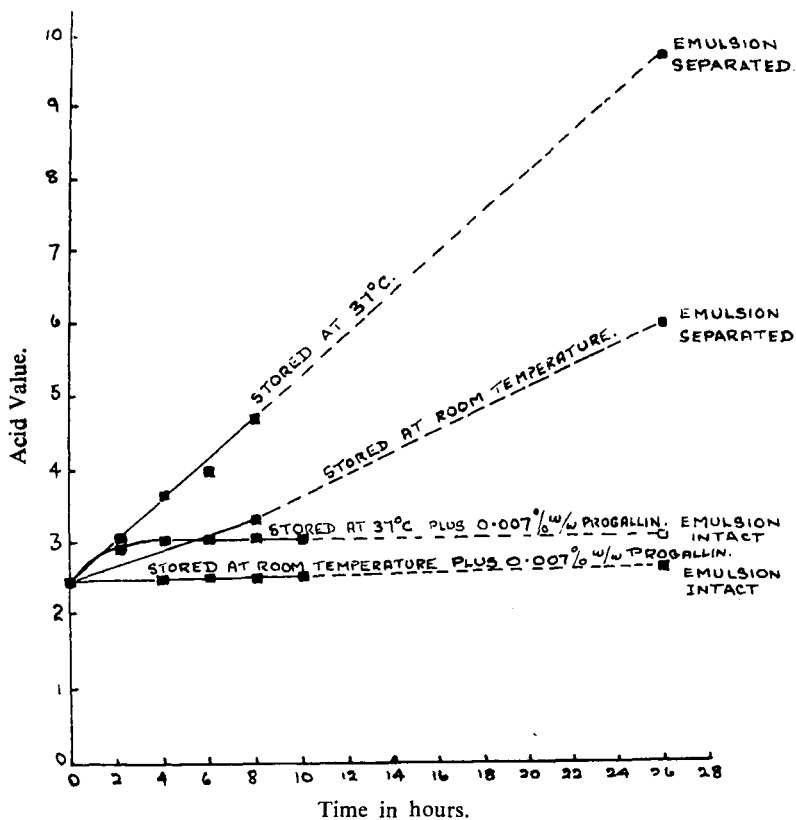


FIG. 4.

### METHODS USED FOR THE DETERMINATION OF PHYSICAL AND CHEMICAL CONSTANTS

Acid value, cholesterol (digitonide method), and saponification value were determined by the method described in the British Pharmacopoeia 1948.

*Acetyl value.* The method described in the British Pharmacopoeia 1948, page 762, was found inconvenient for ordinary samples of wool alcohols and could not be applied at all to highly oxidised samples since the high viscosity of the acetylated material rendered its washing and recovery from the separating funnel extremely difficult. The following modification was therefore devised and proved satisfactory in use. After acetylation according to the B.P. method, the mixed acetates were

dissolved in chloroform, filtered and the extract washed with brine until neutral. After finally washing with water and drying over anhydrous sodium sulphate the solvent was removed. The determination was then completed in the normal manner.

*Determination of surface activity by measurement of interfacial tension.* Interfacial tension measurements were undertaken in an attempt to assess quantitatively any changes of emulsifying power which wool alcohols may have undergone as a result of oxidation. Heinrich,<sup>4</sup> who well realised the usefulness of this tool for the study of cosmetic emulsions, made use of the pendant drop method for the measurement of interfacial tension. In addition to measurements on total wool alcohols, experiments with fractions were carried out.

The results are set out in Table II.

TABLE II  
INTERFACIAL TENSION VALUES OF SOME WOOL ALCOHOL FRACTIONS

Fraction	Interfacial tension in dynes/cm. Age of interface 120 secs.
Total wool alcohols (1 per cent. w/v in white oil*)	5.0
Cholesterol (1 per cent. w/v in white oil)	5.6
iso-Cholesterol (1 per cent. w/v in white oil) (Lanosterol-agnosterol fraction)	16.4
Cetyl alcohol (1 per cent. w/v in white oil)	13.8
Blank using water and white oil	52.5
Total wool alcohols (1 per cent. w/v in benzene)	7.4
Optically inactive alcohols (1 per cent. w/v in benzene)	12.4
Blank using water and benzene	32.2

\* Viscosity 74 seconds Redwood

The possibilities of this method were extensively investigated by Andreas *et al.*<sup>5</sup> whose techniques and calculations have been freely adopted in our work. Certain mathematical functions necessary for the application of their technique have recently been published in an improved form by Fordham<sup>6</sup> whose tables have been used throughout this study.

The method consists of developing a suitably shaped drop of one phase beneath the surface of the other. From measurements of the drop aided by suitable magnification the interfacial tension of the particular system can be calculated. The apparatus is illustrated in Figure 5 and is substantially that used by Andreas *et al.*<sup>5</sup>. Certain features of difference will be described to supplement the diagram.

1. The lighting was obtained from a high power microscope lamp using 6 volt 8 amp. bulbs and fitted with adjustable lenses and an iris diaphragm.

2. The drops were expelled from a glass jet of suitable size by means of a 10 ml. hypodermic syringe fitted with a micrometer adjustment. A similar device had been used by Smith.<sup>7</sup>

3. The constant temperature cell was mounted together with the drop-forming mechanism in place of the stage of a microscope, the barrel being horizontal, so that multi-directional adjustment could be easily obtained. The camera was a Kodak  $\frac{1}{4}$  plate, fitted with Compur shutter and ground glass focussing back. In practice it was found that suitable magnification to cover the different sizes of drops could be obtained by the use of 1 inch or  $\frac{2}{3}$  inch microscope objectives.

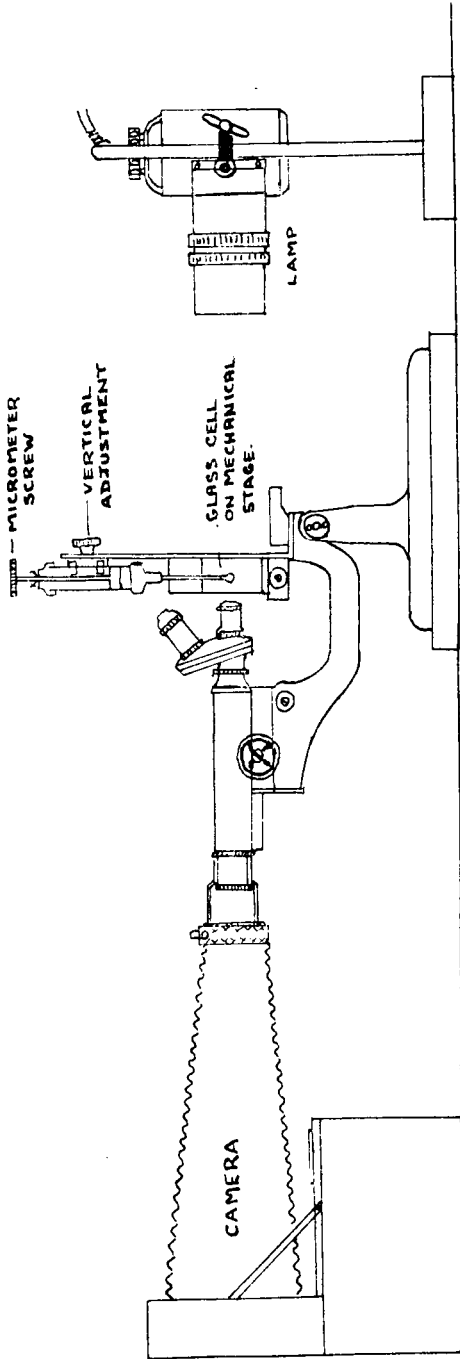
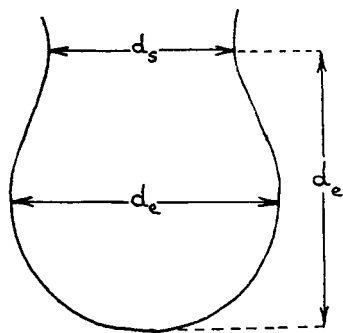


Fig. 5. Apparatus for the measurement of interfacial tension.



Briefly the experimental procedure was as follows:—The sample of wool alcohols under test was accurately weighed out dissolved in benzene\* and adjusted to volume to give a 1 per cent. w/v solution. The solution was placed in the glass cell of the apparatus and drops of water contained in the syringe were developed on the end of a suitable jet as illustrated. The rate at which successive drops were formed was kept as uniform as possible and when the drop had the correct shape (possessed a suitable waist) it was photographed. The drop was photographed at intervals of 60 and 120 seconds after formation, since a finite time is necessary for the establishment of the interface and the attainment of a minimum value of interfacial tension. The plate was placed in a photographic enlarger and projected on to squared paper. The dimensions needed for the calculation were then measured directly and the interfacial tension calculated using the tables published by Fordham<sup>6</sup> in conjunction with the following formula quoted by Andreas *et al.*<sup>5</sup>:—

$$\gamma = \frac{(\rho^1 - \rho^2) \times g d_e^2}{H} \qquad S = \frac{d_s}{d_e}$$



where  $\gamma$  = interfacial tension in dynes per cm. between the two phases under consideration  $\rho^1 - \rho^2$  = difference in densities of the two phases at the temperature of the experiment.  $g$  = acceleration due to gravity.  $H$  = function of  $S$ , which can be obtained from the  $HS$  functions for pendant drops given by Andreas *et al.*<sup>5</sup> and Fordham.<sup>6</sup> For a derivation of this relationship the original paper by Andreas *et al.* should be consulted.

#### DISCUSSION

The composition of wool alcohols has been the subject of study by a number of workers and although a full analysis has not been completely worked out for any one specimen of the material, it is fairly clear that it consists essentially of a mixture of optically inactive aliphatic alcohols, the most prevalent of which is ceryl alcohol,<sup>8</sup> sterols, principally cholesterol<sup>9</sup>, and triterpenes<sup>10</sup> (essentially a mixture of two triterpene alcohols lanosterol and agnosterol, originally termed 'isocholesterol' by Schulze<sup>11</sup>).

Gillam<sup>3</sup> in his paper has suggested that wool alcohols on oxidation produce a mixture of fatty acids, esters and alcohols, and infers that sterols are primarily concerned in the degradative changes involved. We are of the opinion that evidence obtained by Gillam,<sup>3</sup> coupled with that obtained by ourselves in this study, is insufficiently complete to elucidate the mechanism of the degradation of wool alcohols resulting from

\* Benzene was used in this series of experiments since oxidised samples of wool alcohols become increasingly insoluble in liquid paraffin which was used in the preparation of emulsions.

## WOOL ALCOHOLS. PART I

oxidation. Our results show, however, that the material is readily prone to oxidation. These findings appear to be at variance with statements by Lower<sup>2</sup> that wool alcohols are extremely resistant to oxidation and do not decompose or go rancid. A progressive rise in acid value, coupled with the fall in acetyl value and rising ester value, suggests that wool alcohols as a result of oxidative degradation become partially converted into carboxylic acids which can then undergo esterification either with unchanged fractions of the wool alcohols or their oxidation products which have retained a functional hydroxyl group. Such a mechanism has already been envisaged by Gillam.<sup>3</sup> A steady fall in the precipitable digitonides suggests that the sterols are involved in one or other of these degradations. For example, the increase in ester value and the steady fall in yield of the precipitable digitonides are linearly related, and Figures 6, 7 and 8 indicate the interdependence of some of the changes

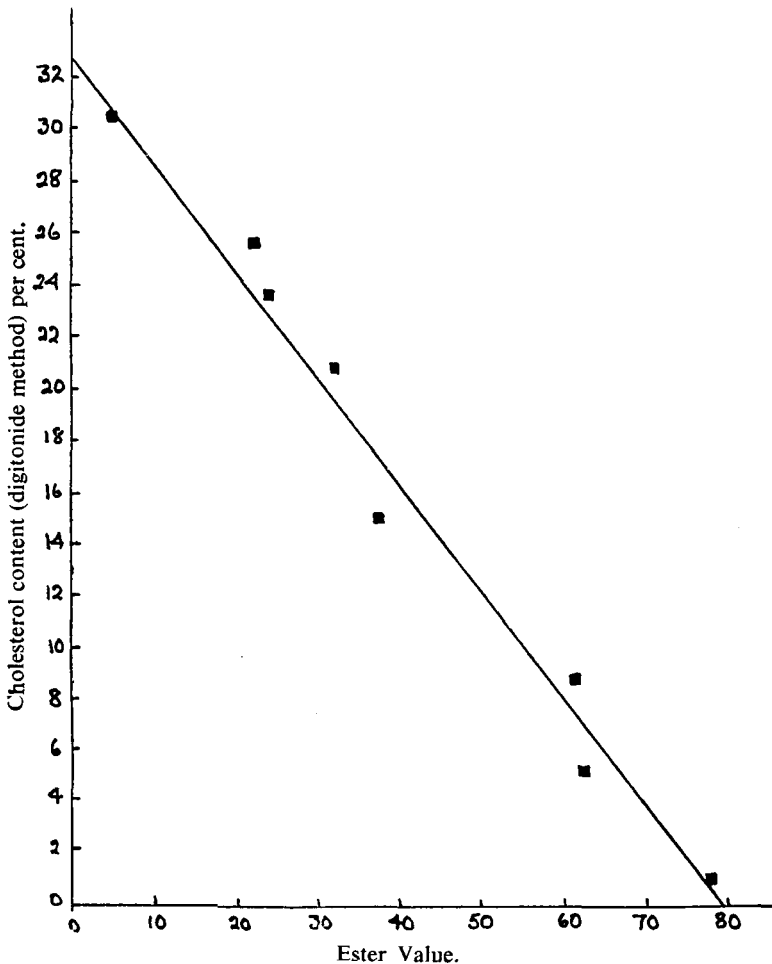


Fig. 6.

we have observed. It is interesting to note that the oxidised wool alcohols appear to show changes in physical properties which are suggestive of polymerisation, thus the material becomes increasingly vitreous and viscous, its melting point rises and its solubility in certain hydrocarbons decreases.

It is not proposed to elaborate however on possible mechanisms of degradation with the limited data which is available at this stage of the work. Further investigations on this subject will appear in subsequent communications.

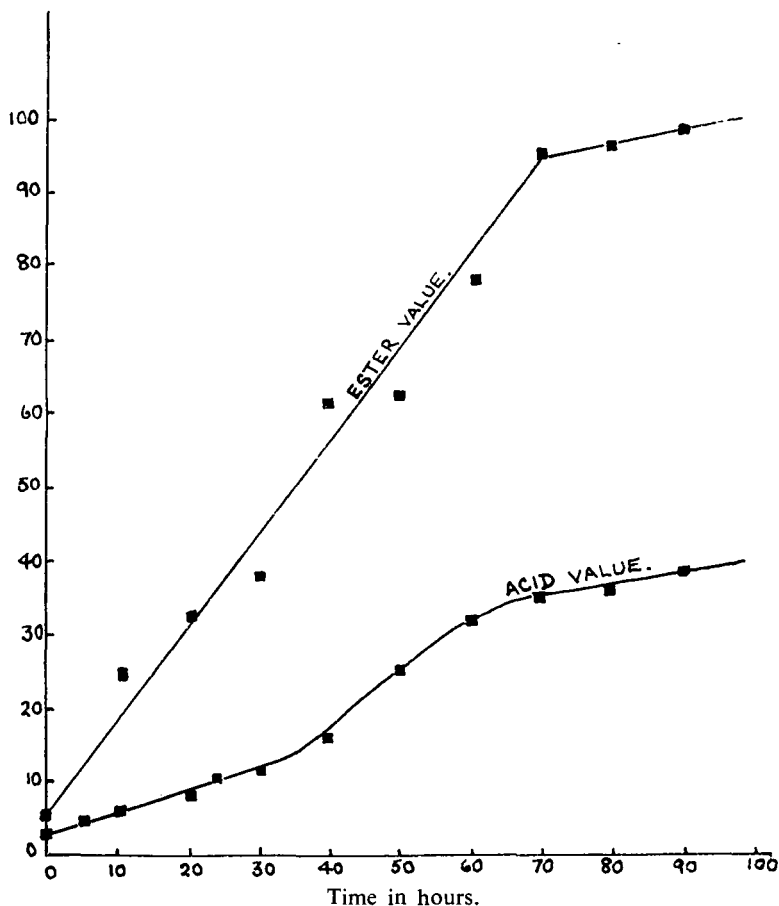


FIG. 7.

Interfacial tension measurements when carried out in a solvent in which samples at all stages of oxidation are completely soluble, show an initial fall with the attainment of a steady value when other chemical changes have become negligible. This suggests that wool alcohols do not suffer a deterioration of surface activity on oxidation. Their diminished efficiency as an emulgent may be attributable to loss of solubility in the hydrocarbon phase of the emulsion. The observations

concerning antioxidants are of interest and may be of practical value in the preservation of wool alcohols and emulsions prepared therefrom.

## SUMMARY

1. Wool alcohols have been subjected to oxidation under varying conditions and progressive changes in physical and chemical properties have been observed. Such changes include—rise in acid and saponification value, decrease in acetyl value and cholesterol content.

2. The interfacial tension-reducing power of total wool alcohols and some isolated fractions have been measured using the pendant drop method. This value does not show any appreciable change as oxidation proceeds.

3. Wool alcohol emulsions suffer breakdown on storage. This is accompanied by rise in acid value of the oil phase. Both effects

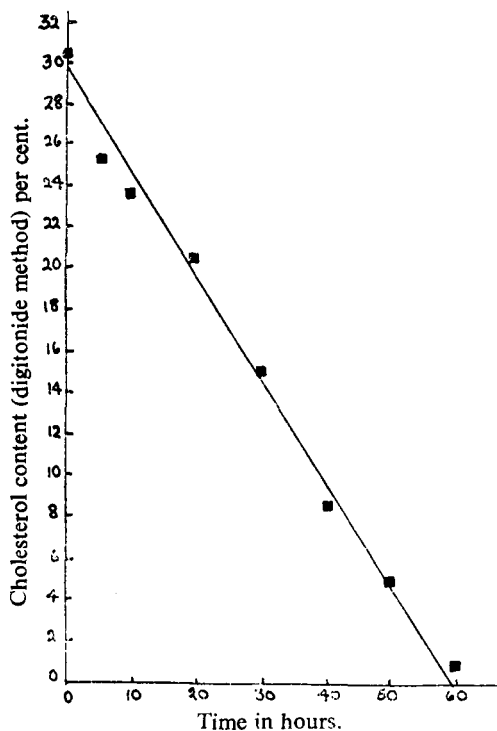


FIG. 8.

can be retarded by the inclusion of antioxidants in the formula.

4. Some tentative mechanisms based on the results obtained have been put forward to explain the changes which wool alcohols undergo on oxidation.

Much of the practical work was carried out by Miss E. Graydon, P. Hills and G. Sumpter. The authors wish to thank A. G. Wright for his work in connection with the design and construction of the two types of apparatus illustrated and the Directors of Herts Pharmaceuticals Limited for permission to publish this work.

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