# AUTOXIDATION, AND ITS INHIBITION, IN ANHYDROUS LANOLIN

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Long-term storage tests under good and bad conditions, and accelerated active oxygen method tests, have shown that autoxidative degradation of anhydrous lanolin can be satisfactorily inhibited for at least 32 months under good conditions or 2 years under bad conditions by 100 p.p.m. of butylated hydroxytoluene or butylated hydroxyanisole. Good results from other antoxidants, and disadvantages of some, are reported. Different lanolins are affected to different degrees, possible reasons being suggested, but autoxidation when uninhibited does not penetrate deeper than 1 cm. even after 2 years of adverse conditions; there is a fall in melting point and formation of up to 4·7 per cent of water-soluble substances including low-molecular weight acids. Absence of change in iodine value and rapid increase of acidity in darkness are contrary to previous reports.

Although oxidation of Anhydrous Lanolin (referred to hereafter as "lanolin"), its precursors and components has been previously studied,* most of this valuable work was based on accelerated oxidations or relatively short-term natural oxidation, or involved foreign lanolin refined by different processes to those used in this country, or reported changes only in acidity and peroxide value without distinction between surface and overall effects. It did not include long-term natural storage tests under good and bad conditions with a range both of antoxidants and concentrations in various lanolins. Also there are no reports about the depth to which autoxidation could penetrate, whether antoxidants inhibited other changes apart from those in acidity and peroxides, or whether there was similarity between the results of natural and accelerated oxidation of pharmaceutical lanolin.

Such investigations have therefore been made, using antoxidants recognised as innocuous (Ward, 1959; Min. of Food, 1954; Stat. Instr., 1958). Three experimental techniques have been used because (i) use of a single large container for storage tests limited the samples obtainable from the original, undisturbed surface and caused frequent changes of the air, (ii) use of many individual containers meant that they must be small, with potential errors because of differences in tightness of sealing and (iii) many antoxidant systems were involved.

* Clark and Thomas, 1949; Drummond and Baker, 1929; Freney, 1940; Gillam, 1948a; Gilmore, 1934; Horn, 1958; Horn and Ilse, 1956; Janecke and Senft, 1957a; Lewkowitsch, 1904; Lifschutz, 1924; Möllering, 1931; Muirhead and others, 1949; Nitschke, 1959; Peereboom, 1959; Ryberg, 1937; Salomone, 1930; Sandell, 1948, 1950; Windaus and others, 1941; Woodmansey, 1919.

## EXPERIMENTAL

### *Storage in Closed Jars at Room Temperature*

*Lanolins used.* (*a*) B.P., superfine; (*b*) and (*c*) B.P., Standard, (*d*) D.A.B. 6, Superfine, all of British manufacture*, and (*e*) D.A.B. 6 of German manufacture.†

*Antoxidant systems used* (*concentrations in p.p.m.*) (i) ±-α-tocopherol‡ 77, ascorbyl palmitate‡ 23; (ii) ±-α-tocopherol 20, ascorbyl palmitate 70, citric acid 10; (iii) butylated hydroxyanisole (B.H.A.)§ 100, propyl gallate¶ 30, citric acid 20; (iv) propyl gallate 500; (v) ±-α-tocopherol 100; (vi) B.H.A. 500; (vii) B.H.A. 200; (viii) B.H.A. 50; (ix) butylated hydroxytoluene (B.H.T.)* 500; (x) B.H.T. 200; (xi) B.H.T. 50; (xii) ±-α-tocopherol 50; (xiii) ±-α-tocopherol 20.

[Synergistic effects of citric acid (Janecke and Seft, 1957a; Stirton and others, 1945; Mattil, 1945), and system (iii) (Kraybill and others, 1948), were previously reported].

All but two of the antoxidants were dissolved in a little hot lanolin, the resultant concentrate being thoroughly mixed with the just-molten bulk. The exceptions, citric acid and propyl gallate, were dissolved in the minimum hot distilled water and stirred into the molten lanolin which was then homogenised. Each of the resultant lanolins was poured whilst still molten into amber glass jars of approximately 100 g. capacity. These were tightly closed by lacquered tin-plate screw caps with compressed paper wads, and packed into cardboard cases to exclude light completely. The storage temperature fluctuated between 4 and 25°.

*Methods of examination.* During the early stages of storage one jar from each test system was taken at monthly intervals for examination and analysis, later the intervals were increased. The surface of the contents of each jar was carefully removed with a flat scraper, 11 g. being taken. The average depth removed was approximately 7 mm., i.e. 18 per cent of the total depth. The surface portion and remainder of each sample were separately melted and stirred before analysis, the following tests being applied to both.

(1) Acid value: the method of the B.P. 1958.

(2) Iodine value: the method of the B.P. 1958 specified for Anhydrous Lanolin (iodine monochloride method).

(3) Saponification value: the method of the B.P. 1958, extending the time of reflux to 4 hr. and adding a little purified carborundum as boiling-aid.

(4) Peroxide value: the simplified Lea (1938) method, expressing results as ml. of N/500 thiosulphate per g. of sample.

* "Golden Dawn", Westbrook Lanolin Company.

† "Goldenes Vliess", Woll-Wäscherei und Kämmerei in Döhren bei Hanover.

‡ Roche Products Ltd.

§ "Tenox", Kodak Ltd., and "Embanox", May & Baker Ltd.

¶ "Progallin", Nipa Laboratories Ltd.

* "Shell Antiodixant T.P. 6335", Shell Chemical Co. Ltd.

(5) Melting point: the method of the B.P. 1958, but to avoid cold-working errors the cups were filled with molten lanolin and allowed to stand 24 hr. at room temperature before the determination.

(6) Colour: measured whilst molten by an EEL photoelectric colorimeter using blue and green filters. Results were converted by a calibration graph to equivalent Lovibond Yellow and Red units for a $\frac{1}{4}$ in. cell.

(7) Total cholesterol: the Liebermann-Burchard method, measuring the intensity of colour on an EEL photoelectric colorimeter with a red filter. A gravimetric precipitation by digitonin from the original lanolin (after conversion of esterified cholesterol to the free state) was used as

TABLE I

CHANGES IN SURFACE LAYER OF D.A.B. 6 SUPERFINE LANOLIN (BRITISH) DURING STORAGE IN PART-FULL CANS

| | Original results | Results after 2 years with antoxidant system: Control | (i) | (ii) | (iii) | (iv) | (v) | (vi) |
|---|---|---|---|---|---|---|---|---|
| Acid value | 0·24 | 9·46 | 5·42 | 3·64 | 0·30 | 0·38 | 6·64 | 0·30 |
| Saponification value | 97·5 | 107·0 | 104·0 | 106·8 | 98·0 | 98·0 | 111·3 | 96·0 |
| Ester value | 97·3 | 97·5 | 98·6 | 103·2 | 97·6 | 97·5 | 104·7 | 95·6 |
| Peroxide value | 11·0 | 166·0 | 157·0 | 149·0 | 12·0 | 9·0 | 237·0 | 12·0 |
| Iodine value | 28·0 | 24·4 | 22·9 | 25·4 | 27·0 | 29·1 | 24·0 | 26·9 |
| Unsaponifiables, per cent | 51·0 | 44·7 | 47·6 | 42·9 | 52·1 | 49·9 | 43·0 | 53·4 |
| Total saponifiables, per cent | 50·0 | 52·1 | 53·2 | 56·3 | 50·0 | 52·0 | 56·9 | 48·4 |
| Total recovery, per cent | 101·0 | 96·8 | 100·8 | 99·2 | 102·1 | 101·9 | 99·9 | 101·8 |
| Total cholesterol, per cent (Liebermann-Burchard) | 20·8 | 14·0 | 12·1 | 15·5 | 18·9 | 18·3 | 13·2 | 18·3 |
| Total cholesterol, per cent (Digitonin) | 20·8 | 13·3 | 14·2 | 13·5 | 19·5 | 17·2 | 10·3 | 19·6 |
| Melting point (°C) | 38·2 | 35·7 | 37·8 | 36·8 | 38·0 | 37·4 | 37·6 | 37·7 |
| Colour | 4·6Y: 0·4R | 4·1Y: 0·4R | 4·8Y: 0·5R | 4·2Y: 0·6R | 3·3Y: 0·4R | 6·9Y: 0·8R (originally 6·8Y: 0·9R) | 3·3Y: 0·4R | 4·1Y: 0·6R |

calibration. These two methods are affected by other steroids or oxidative degradation products which may be present, therefore the results given are not strictly accurate.

The full range of tests was made on samples (*c*) and (*d*) and since little, if any, change appeared to be occurring in other characteristics, acidity and peroxide values only were determined on most of the older samples. With samples (*a*) and (*b*) tests were further confined to the surfaces.

Additional observations were made about the effect of surface autoxidation on permanganate tests and the development of tallowy odour and tough skin.

*Storage at Room Temperature in Part-full Cans*

*Lanolins and antoxidant systems used.* Lanolins (*c*) and (*d*) and Systems (i) to (vi) were used.

*Method.* Standard cylindrical tin-plate cans of 5 kg. capacity were filled with molten lanolin to the 4 kg. level only, leaving an abnormally large air space to represent bad storage conditions. The filled cans with lids applied in the normal way were stored undisturbed for 2 years as previously described, before being examined.

*Examination of the surface.* The lanolin within a lightly-inscribed circle of 3 in. (76 mm.) diameter was carefully removed to a depth of $\frac{1}{8}$ in. (3·2 mm.) by a spatula and melted and mixed. The tests previously described were applied and in addition, ester values were calculated and

TABLE II

PENETRATION OF AUTOXIDATION IN D.A.B. 6 SUPERFINE LANOLIN (BRITISH) DURING STORAGE IN PART-FULL CANS

| Depth of sample (in.) | Original acid value | Acid value after 2 years with antoxidant system: | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Control | (i) | (ii) | (iii) | (iv) | (v) | (vi) |
| 0–$\frac{1}{8}$ | 0·24 | 9·46 | 5·42 | 3·64 | 0·30 | 0·38 | 6·64 | 0·30 |
| $\frac{1}{8}$–$\frac{1}{4}$ | — | 0·82 | 0·98 | 0·78 | 0·30 | 0·30 | 0·82 | 0·28 |
| $\frac{1}{4}$–$\frac{3}{8}$ | — | 0·40 | 0·42 | 0·44 | — | — | 0·36 | — |
| $\frac{3}{8}$–$\frac{1}{2}$ | — | 0·29 | 0·30 | 0·40 | — | — | 0·29 | — |
| $\frac{1}{2}$–$\frac{5}{8}$ | — | 0·29 | 0·30 | 0·29 | — | — | 0·29 | — |
| $\frac{5}{8}$–$\frac{3}{4}$ | — | — | — | 0·30 | — | — | — | — |

unsaponifiables and total saponifiables determined. The results for unsaponifiables were corrected for any soap content resulting from incomplete extraction and the corrections added to the figures for total saponifiables. The latter were determined and not calculated by subtraction of the unsaponifiables from 100 per cent.

*Examination of the lower layers.* After removal of the upper $\frac{1}{8}$ in., successive depths of $\frac{1}{8}$ in. were removed from the same area. Each

TABLE III

PENETRATION OF AUTOXIDATION IN D.A.B. 6 SUPERFINE LANOLIN (BRITISH) DURING STORAGE IN PART-FULL CANS

| Depth of sample (in.) | Original peroxide value | Peroxide value after 2 years with antoxidant system: | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Control | (i) | (ii) | (iii) | (iv) | (v) | (vi) |
| 0–$\frac{1}{8}$ | 11 | 166 | 157 | 149 | 12 | 9 | 237 | 12 |
| $\frac{1}{8}$–$\frac{1}{4}$ | — | 33 | 41 | 26 | 12 | 10 | 42 | 13 |
| $\frac{1}{4}$–$\frac{3}{8}$ | — | 13 | 8 | 12 | — | — | 12 | — |
| $\frac{3}{8}$–$\frac{1}{2}$ | — | 8 | 10 | 9 | — | — | 12 | — |
| $\frac{1}{2}$–$\frac{5}{8}$ | — | 9 | 10 | 11 | — | — | — | — |
| $\frac{5}{8}$–$\frac{3}{4}$ | — | — | — | — | — | — | — | — |

portion was separately melted and mixed before being tested for acidity and peroxide value. Removal of portions was continued until there was no further change in characteristics.

## RESULTS AND DISCUSSION

Many of the graphs of results from storage in closed jars at room temperature showed large fluctuations. Whilst peroxide values may reach a maximum and then decrease as the rate of decomposition of peroxides exceeds the rate of formation (Paschke and Wheeler, 1944), it is almost inconceivable that a value should re-approach the original one whilst oxidisable matter still remains, or that decomposed cholesterol should be regenerated. We have assumed that sudden falls in a graph resulted from lack of oxidation because of a high degree of sealing of some jars. With efficient antoxidant systems instances of sudden fluctuations were few and effects were slight, and changes in all chemical and

physical characteristics were satisfactorily inhibited for the duration of the tests.

*Acid value: peroxide value.* Increases in these values were the most significant effects of autoxidation, Figs. 1–4 typify the results obtained. Other comparative tests followed a similar trend although the increases were smaller. In many instances, including samples which had suffered negligible surface oxidation, there appeared to be a very slight increase

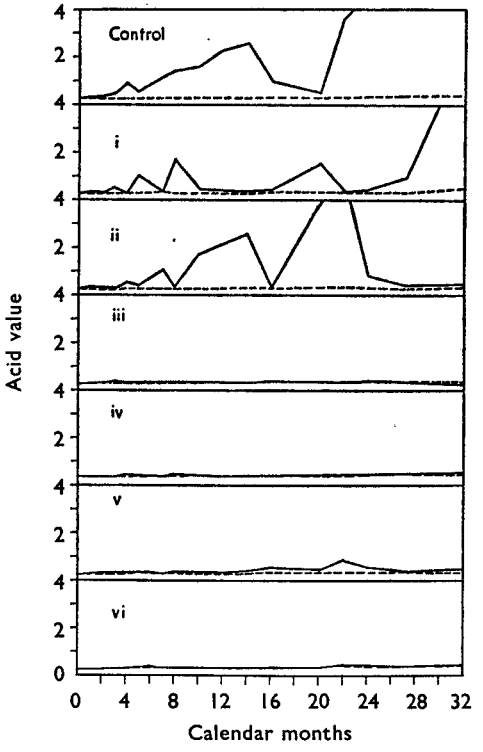


FIG. 1. Change in acid value of lanolin (sample (d)) stored in jars.
—— Surface layer - - - - Underlying bulk.

in acid value of the bulk after long storage, suggesting a gradual hydrolysis of the lanolin esters.

*Iodine Value.* Changes were negligible, even in highly oxidised samples, and are therefore not reported. These findings contradict those of Salomone (1930) but may be explained by other work (Bergström, 1943; Gillam, 1948b; Gunstone and Hilditch, 1945; Horn, 1958; Horn and Ilse, 1956; Keller and Weiss, 1950; Weiss and Keller, 1950).

*Saponification value: ester value.* Increases in both occurred, indicating esterification or condensation of many of the acids produced by autoxidation similar to previously-reported results of accelerated oxidation. The fall in total recovery, i.e. unsaponifiables plus total saponifiables, from the normal value of over 100 per cent indicates that up to 4·7 per

cent of water-soluble by-products may be present in highly oxidised lanolin. Some of these by-products are indicated to be acids of relatively low molecular weight since an aqueous extract of the oxidised lanolin invariably had a low pH.

*Melting point.* Although badly oxidised surfaces of lanolin consisted of tough skins the melting points found were lower than those of the corresponding bulks (Muirhead and others, 1949; Clark and Kitchen, 1960). The decreases found initially being small, are not reported.

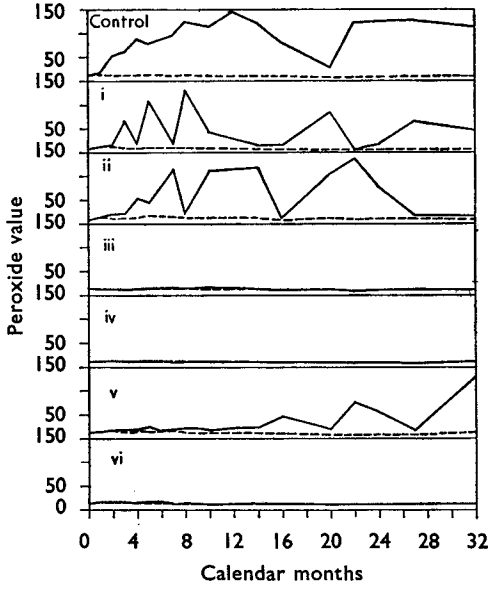


FIG. 2. Change in peroxide value of lanolin (sample (d)) stored in jars.
—— Surface layer - - - - Underlying bulk.

*Colour.* Bleaching of autoxidised surfaces was found, and is normal although some lanolins of German manufacture have been known to darken (also reported by Salomone, 1930). The addition of the larger concentrations of propyl gallate brought an immediate darkening in colour.

*Cholesterol content.* The autoxidative degradation found agrees with previous work except that of Norcia (1958). In some instances the lower bulk of a sample showed a very slight decrease (of doubtful significance) in cholesterol content.

*Permanganate test.* The effect of autoxidation upon a permanganate test as specified for lanolin by several pharmacopoeias has already been studied (Sandell, 1950). Initially permanganate tests were made at irregular intervals, and the results showed that the surface of lanolin which originally complied began to fail the test (the D.A.B. 6 method was used) in 2 to 3 months, the lower bulk remaining unaffected. Efficient antoxidants prevented formation of permanganate-reducing substances

until other chemical changes became detectable. Sandell (1950) reported that the incorporation of propyl gallate in lanolin adversely affected the permanganate test because of aqueous solubility. We confirmed this effect and found it to extend also to B.H.A. and citric acid, the initial effect of B.H.A. being slight but increasing with age. B.H.T. and α-tocopherol did not have the effect.

*Odour and skin formation.* A tallowy odour and hard skin were found only in samples which showed significant chemical changes. The

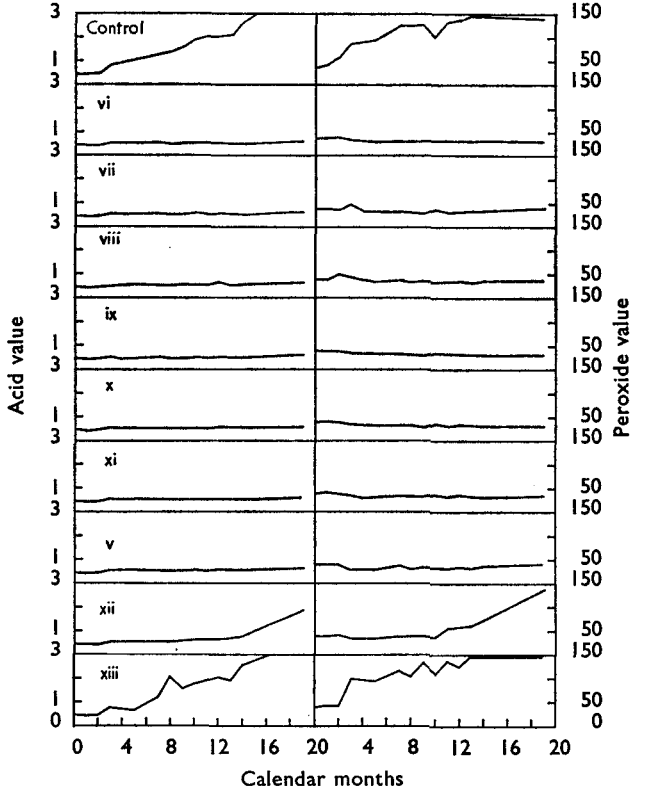


FIG. 3. Changes in acid value and peroxide value of lanolin stored in jars (sample (*a*); surface layer only).

first change in odour was apparent after 3 months, and the first definite skinning after 5 months.

*Light.* Contrary to Möllering's (1931) findings the results show that complete absence of light does not prevent autoxidative increase in acid value.

*Differences in rates of oxidation.* Differences in rates of oxidation between different types of crude wool fat have been noted previously. With refined lanolin, the peroxide and acid values in particular showed that the samples differed greatly in their response to both oxidation and

antoxidants, even though processes used in refining the British lanolins had differed in only minor ways. Possible reasons are: (i) Differences in content of trace metals such as copper and manganese which can act as oxidation catalysts (King and others, 1933b; A.O.C.S., 1945). Although manganese compounds have been isolated from wool fat (Truter and Woodford, 1954) the amounts in high quality pharmaceutical lanolin are minute. (ii) Variation in traces of phosphorus compounds. These have been found in lanolin by Drummond and Baker (1929), Janistyn

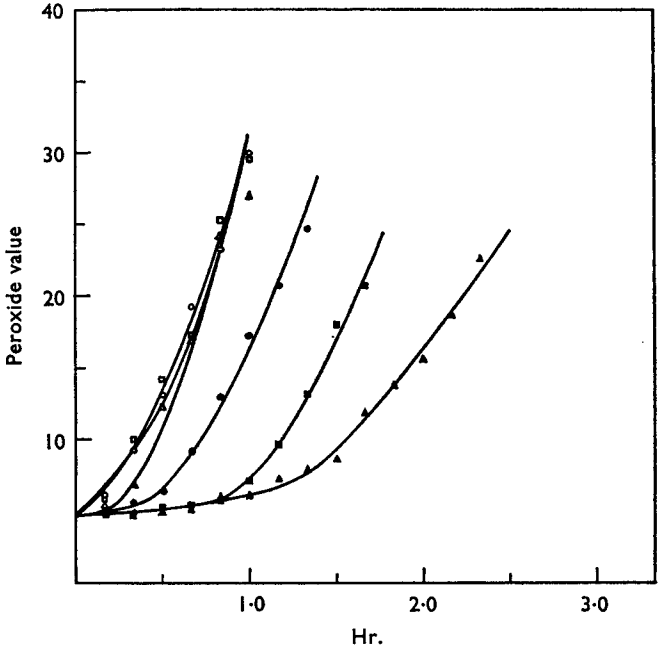


FIG. 4. Active oxygen method tests on lanolin. The antoxidant effect of ±-α-tocopherol.
○ control. □ 10 p.p.m. △ 40 p.p.m. ● 100 p.p.m. ■ 200 p.p.m. ▲ 500 p.p.m.

(1940a,b), and Janecke and Senft (1957b), and the effect of phosphatides on oxidation of oils has been reported by Braae (1958). (iii) Existence of natural antoxidants in raw wool fat, variable quantities being carried through the refining processes into the finished lanolin. (iv) The catalytic effect of peroxides already in the lanolin. The order of susceptibility to oxidation found was not apparently related to the original peroxide values. (v) Differences in previous history of the lanolins. Although raw wool fat on the fleece oxidises extensively the principal oxidation products are removed during refining, but traces of some substances may remain and promote subsequent oxidation to varying degrees. (vi) Differences in pH. We have found that minor details in processing which affect the pH of an aqueous extract of the finished lanolin may also affect its general stability.

## EXPERIMENTAL. II

*Active Oxygen Method.* The active oxygen method (A.O.M.) (Wheeler, 1932; King and others, 1933a) involves passing air at a controlled rate through the sample at a controlled temperature. In the present work progress of oxidation was followed by determining the increase in peroxide value.

The apparatus comprised a liquid paraffin heating bath surrounding a 1 l. three-necked reaction flask; a mechanical pump which drew purified air through a pre-heating coil in the paraffin bath, through the molten lanolin in the flask, and finally through a flowmeter. The rate of air

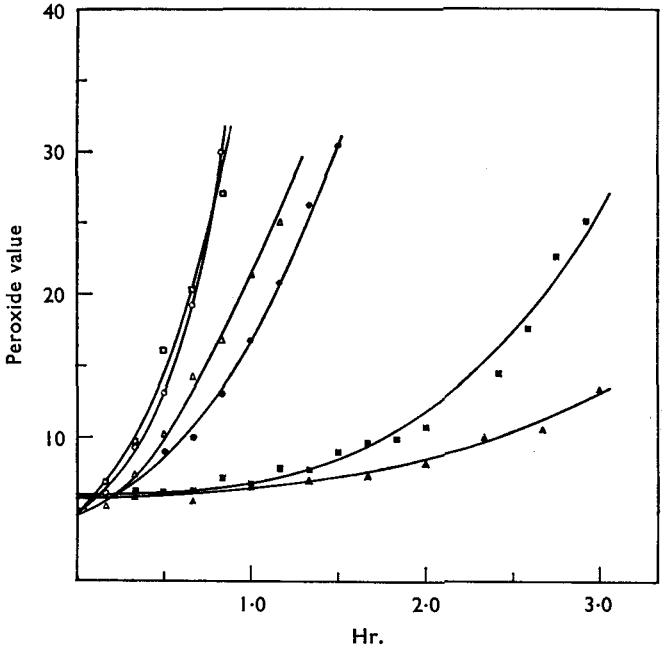


FIG. 5. Active oxygen method tests on lanolin. The antoxidant effect of butylated hydroxyanisole.
○ control. □ 1 p.p.m. △ 5 p.p.m. ● 10 p.p.m. ■ 40 p.p.m. ▲ 100 p.p.m.

flow was controlled at 180 ml./sec. although small variations in rate did not appear to affect significantly the rate of oxidation.

A test involved first heating the bath to about 92°. Meanwhile 200 g. of lanolin were separately heated to 90° and any antoxidant, dissolved in 1 ml. of isopropanol, was added immediately before pouring the hot lanolin into the reaction flask whereupon the flow of air was started without delay. A control experiment showed that the isopropanol evaporated within 2 or 3 min. and had very little effect upon oxidation. The contents of the flask were maintained at 90° throughout the test, samples being removed at regular intervals whilst momentarily interrupting the air flow.

The temperature of 90° was adopted after preliminary experiments, the results of which demonstrated the normal accelerating effect of heat upon the rate of oxidation, particularly between 80° and 90°.

*Type of lanolin used.* Lanolin similar to (*d*) in Part I was used throughout, but because of the amount of work and time involved, samples from different production batches were unavoidably necessary. Since it was found that different batches of lanolin varied in susceptibility to oxidation, control tests were used in choosing batches as similar as possible in behaviour. Experiments made with different batches could

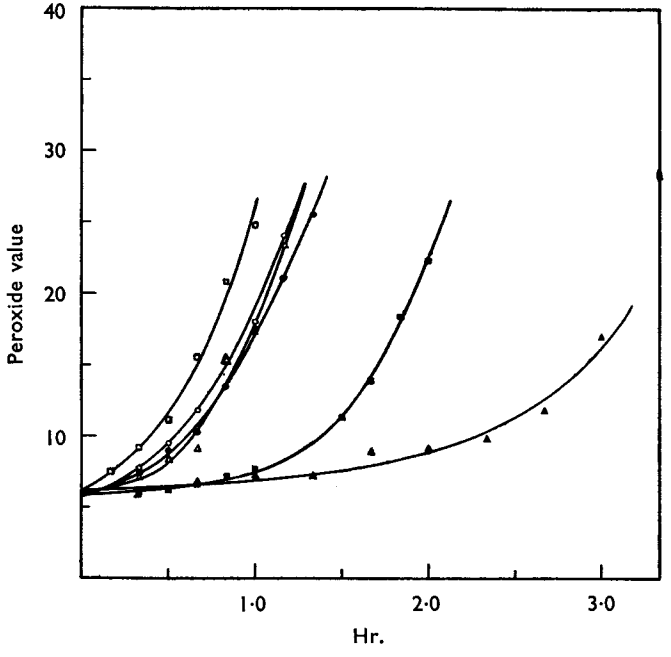


FIG. 6. Active oxygen method tests on lanolin. The antoxidant effect of butylated hydroxytoluene.
○ control. □ 1 p.p.m. △ 5 p.p.m. ● 10 p.p.m. ■ 40 p.p.m. ▲ 100 p.p.m.

not, however, be strictly correlated but series of tests involving a range of concentrations of one antoxidant were always completed on the same lanolin.

*Antoxidant systems used* (*concentrations in p.p.m.*). ±-α-*tocopherol*, 10–500. Also 50–100 plus ascorbyl palmitate (50–200) and citric acid (20–100). B.H.A. 1–40. Also 10 plus citric acid (20–50). B.H.T. 1–40. Also 5–100 plus citric acid (20–100). Ascorbyl palmitate, 50–2000. Citric acid, 20–100.

## RESULTS

Graphs prepared from the results showed very few clearly defined induction periods, most conforming to a basic pattern. Accordingly only typical examples are given in Figs. 4–6.

## Discussion

Since the efficiencies of individual antoxidants were not linearly related to concentration no definite order of efficiency could be established. In general, however, B.H.A. was the most efficient single antoxidant, B.H.T. and propyl gallate almost as good, but α-tocopherol and ascorbyl palmitate much inferior although useful. Ascorbyl palmitate, and particularly citric acid, in addition to having antoxidant properties of their own, strongly augmented the effects of other antoxidants but, whilst in some combinations with α-tocopherol and B.H.A. there appeared to be true synergism, in others the effect may have been merely additive. Ascorbyl palmitate actually reduced peroxides already present in the lanolin at the expense of darkening the colour; at low concentrations ($\leqslant$200 p.p.m.) it had a pro-oxidant effect (Ward, 1959; Baltes, 1955; Baltes and Volbert, 1955), as did also B.H.T. ($\leqslant$5 p.p.m.).

Concerning all the antoxidants tested, the same approximate order of efficiency prevailed throughout, and where results overlapped they agreed fairly well with previous work. We found, however, ascorbyl palmitate and citric acid to be more efficient than did Janecke and Senft and also found a more marked superiority of B.H.A. over α-tocopherol.

Since B.H.T. had almost the highest efficiency and was free from any disadvantages in respect of solubility, colour, permanganate test and acidity, it is indicated to be the most suitable general-purpose antoxidant for lanolin, a concentration of 100 p.p.m. being satisfactory.

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