

A NOTE ON AUTOXIDATION AND ITS INHIBITION IN WOOL ALCOHOLS B.P.

BY E. W. CLARK AND G. F. KITCHEN

From Westbrook Lanolin Company, Argonaut Works, Laisterdyke, Bradford, 4

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The effects on Wool Alcohols B.P. of gradual autoxidation during storage at room temperature have been compared with the known effects of accelerated oxidation. There is a decrease in emulsification value, a bleaching of the surface, and, contrary to previous reports, a rapid fall in melting point. Autoxidation, even under bad conditions, has been inhibited, apart from a slight fall in melting point, for at least 23 months by the addition of 500 p.p.m. of butylated hydroxyanisole, but certain other antioxidant systems had only a limited effect.

THE oxidation of Wool Alcohols B.P. has been studied by a number of workers¹⁻⁴. Muirhead and others² investigated the antioxidant properties of α -tocopherol and pyrogallol, whilst Janecke and Senft³ used butylated hydroxyanisole, α -tocopherol, citraconic acid, β -conidendrol and nor-dihydroguaiaretic acid.

Accelerated methods of oxidation were used in both of these investigations, ultra-violet irradiation was used by Muirhead and others, while Janecke and Senft used a hot air oven, as did Gillam¹ in studying the oxidation of wool wax alcohols. No previous study of the oxidation and its inhibition of wool alcohols stored for long periods under normal conditions has been reported. This we have done.

EXPERIMENTAL AND RESULTS

The storage tests, over almost 2 years, were made in good and bad storage conditions.

Firstly, 100 g. amber glass jars were almost filled with molten Wool Alcohols B.P.* and securely closed with lacquered, tin-plate screw-caps. Secondly, some of the same batch of wool alcohols was scraped into very thin shavings and packed loosely into similar jars, with loose fitting caps.

Wool alcohols containing four different antioxidant systems and a control were included in the storage tests. The four systems were as follows. (1), ascorbyl palmitate† 77 p.p.m., (\pm)- α -tocopherol (free)† 23 p.p.m.; (2), ascorbyl palmitate 70 p.p.m., (\pm)- α -tocopherol (free) 20 p.p.m., citric acid 10 p.p.m.; (3), (\pm)- α -tocopherol (free) 100 p.p.m.; (4), butylated hydroxyanisole‡ 500 p.p.m.

All but one of the antioxidants were dissolved in a little of the wool alcohols whilst hot, the resultant concentrate being thoroughly mixed into the bulk of the molten alcohols. The exception, citric acid, was dissolved in the minimum of hot water and this solution stirred into the molten alcohols, which were then passed through a piston-type homogeniser.

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

† Supplied by Roche Products, Ltd.

‡ "Embanox," supplied by May and Baker, Ltd.

Methods of Examination

Jars of each test system were removed from storage at regular intervals. The contents of each were melted and mixed, and submitted to the following tests.

1. *Acid value.* The method of the B.P. 1958.
2. *Saponification value.* The method of the B.P. 1958, modified by extending the time of reflux to 4 hours and adding a little purified carborundum powder as an aid to boiling.
3. *Emulsification value.* The per cent by volume of water emulsified at 25° (using a twin-beater, electric food mixer) by a mixture of 5 g. of wool alcohols with 40 g. of Liquid Paraffin B.P.
4. *Melting point.* The method of the B.P. 1958.
5. *Cholesterol content.* Determined colorimetrically by the Liebermann-Burchard reaction. The method was previously calibrated on the same wool alcohols against cholesterol determined by digitonin. Owing to the known interference with this colorimetric method by oxidative degradation products the results are only an indication of the trend of the changes.
6. *Colour.* Determined hot with a Lovibond Tintometer, using a $\frac{1}{4}$ in. cell and measuring yellow and red units. Most samples required the superimposition of neutral tint glasses.

The results are included in Figures 1 to 5.

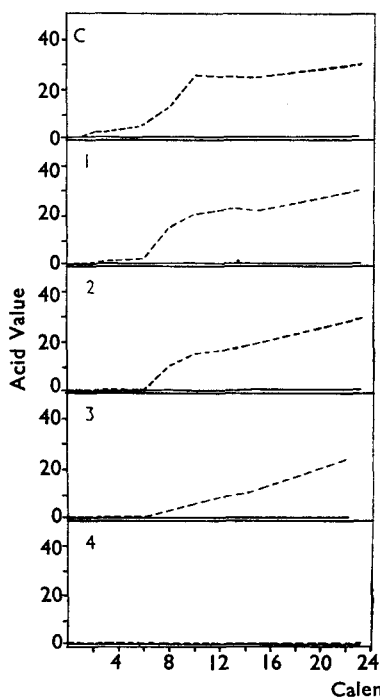


FIG. 1. Changes in acid value.
— Solid wool alcohols.

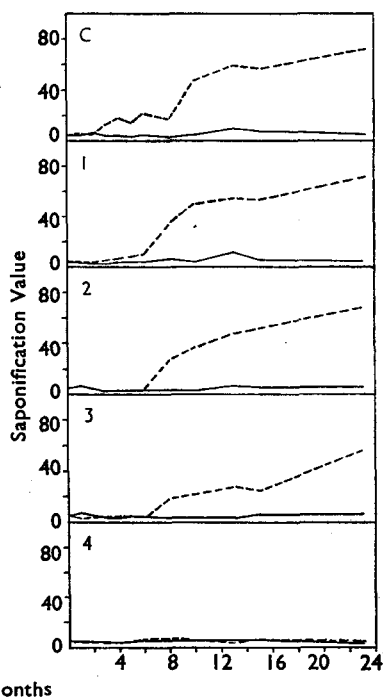


FIG. 2. Changes in saponification value.
--- Flaked wool alcohols.

The numbers in the graphs refer to the systems in the text. C = Control.

AUTOXIDATION IN WOOL ALCOHOLS

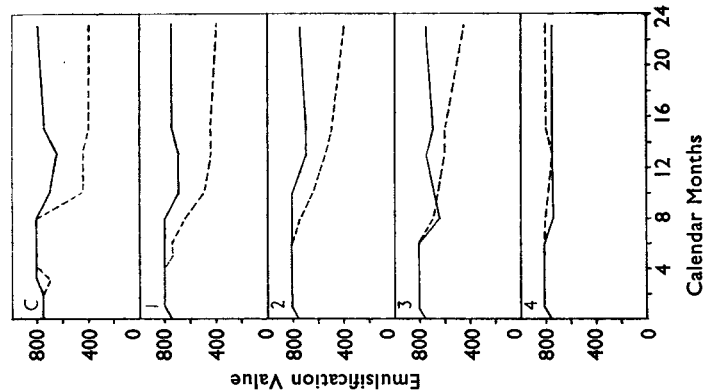


FIG. 3. Changes in emulsification value.
 — Solid wool alcohols.
 - - - Flaked wool alcohols.

The numbers inside the graphs refer to the systems described in the text. C = control.

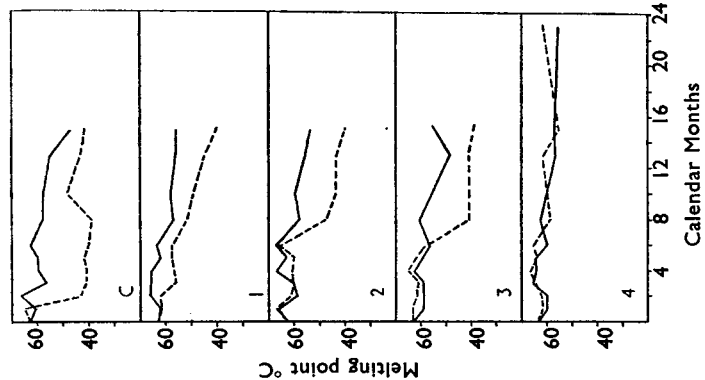


FIG. 4. Changes in melting point. Melting points were not taken after 15 months, owing to the difficulties created by the extremely viscous nature of the molten oxidised samples.

The numbers inside the graphs refer to the systems described in the text. C = control.

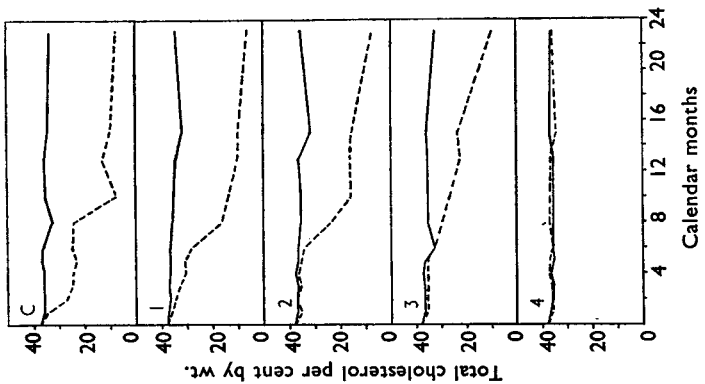


FIG. 5. Changes in cholesterol content.

C = control.

DISCUSSION

The Figures show that the changes in wool alcohols as a result of gradual autoxidation at room temperature are similar to those occurring during accelerated methods of oxidation. When stored under good, normal conditions, however, the autoxidised surface layer is indicated to be extremely shallow even after 23 months. No measurement of the thickness of the layer was attempted, but from visual judgment it was less than 1 mm. Some surface bleaching occurred but light was non-essential for autoxidation.

The results confirm earlier findings that autoxidation may be effectively inhibited by a suitable antioxidant such as butylated hydroxyanisole, using 500 p.p.m., the other antioxidants tested having a very limited effect. Concentrations of butylated hydroxyanisole lower than used here may be sufficiently effective for practical purposes. Janecke and Senft showed 200 p.p.m. to be almost as effective as 500 p.p.m., but further work is contemplated to extend the range of antioxidants tested, and also to determine how the natural susceptibility to autoxidation of wool alcohols varies between different production batches.

REFERENCES

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