MR. L. G. TOWERS : When chromatographing lavender oils at relatively low column temperatures in order to resolve as completely as possible the components of shorter retention times, what do you consider to be the minimum column temperature below which sample preheating becomes necessary ?

THE LECTURER : No significant loss of performance was observed when samples of up to 100 μg were put straight on to a column at 70° C, though at lower temperatures a preheater may be needed. The answer will probably depend upon the size of sample required for the instrument used, but in any case no harm could be caused by a sample preheater at, say, 100° C.

THE DETERMINATION OF WATER IN SHAMPOOS BY DISTILLATION

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Some shampoos, etc., foam excessively on distillation even after the addition of oleic acid. The addition of a quaternary ammonium compound in such cases allows the ready distillation of the water.

INTRODUCTION

THE DETERMINATION of water in shampoos and similar products, by distillation (*Dean and Stark Method*) presents a special problem in that such products normally contain materials of high foaming power, and frequently also a foam stabilizing agent.

Gentle spot heating of the flask just below the liquid surface can often control the foaming by circulating the flask contents and will, at all times, cause a reduction in the amount of foam present. This technique, however, requires the undivided attention of the operator and, with well foaming materials is frequently inadequate. Even when the foaming is kept under control, the solid detergents can set as a cake, as the water distils. If due care is not taken this cake can adhere to the bottom of the flask where it can either occlude water or char. This can lead to low results by the failure of all the water to distil, or to high results due to the water formed by the decomposition. Occasionally, the detergent precipitates as a fine powder which can physically stabilize the foam but, if it does happen, it is usually transient due to the tendency of the powder to agglomerate.

The addition of a non-volatile solvent that will dissolve the anhydrous detergents can reduce, and frequently overcome, these problems. Two such

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solvents that have found favour are glycerine and oleic acid, the latter being preferred by the American Oil Chemists Society (e.g. A.O.C.S. Methods Ca 2b–45 for soaps; and F 1a–44 for sulphated and sulphonated oils).

In this communication a further improvement is reported which allows the ready analysis of very seriously foaming shampoos, etc.

Experimental

To compare the effectiveness of oleic acid and glycerine for control of foaming, the water content of a shampoo was determined using each in turn. Whereas there was no foam with this shampoo when using the oleic acid,

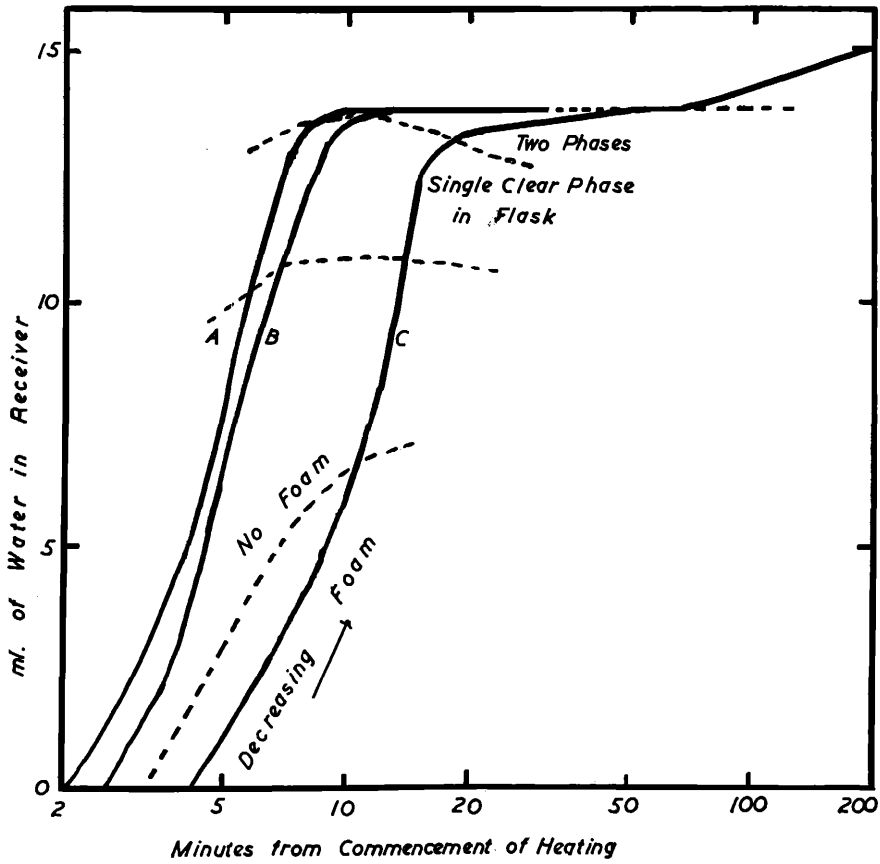

Figure 1

Sample			A	B	C
Shampoo	..	gm	20	20	20
Oleic Acid	..	ml	10	10	nil
Quaternary	..	g	1	nil	nil
Glycerine	..	g	nil	nil	30
Xylene	..	ml	100	100	100

there was considerable initial foam with the glycerine. However, after the first portion of water had distilled the foam subsided and finally ceased. In both cases, the initial slurry in the flask cleared and gave a single phase during the distillation. When further water had distilled, the glycerine separated as a liquid phase which gradually darkened, and which was still evolving water after $3\frac{1}{2}$ hours. On the other hand, in the test with the oleic acid a fine powder separated which rapidly coagulated on the walls of the flask.

The results and the observations of conditions in the flasks are given in *Fig. 1.* (The time scale has been made logarithmic for convenience.)

Other shampoos, particularly those based on the ether sulphates and incorporating alkanolamide foam boosters and stabilizers, are sometimes difficult to analyse due to the excessive and very stable foam even when oleic acid is used. It was found that the addition of a quaternary ammonium compound precipitated some of the anionic detergent and foaming could be eliminated even when the addition was less than stoichiometric.

One such shampoo which proved very difficult to analyse even with the addition of oleic acid, responded perfectly to this treatment, the distillation of water being complete within ten minutes of starting to heat the flask. On the other hand, in the absence of the quaternary, three out of four attempts at the distillation resulted in the contents of the flask foaming

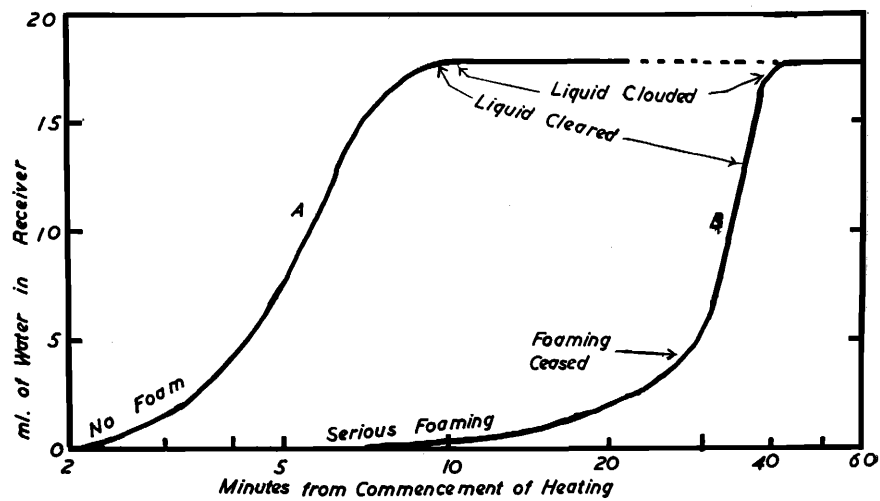

Figure 2

Sample			A	B
Oleic Acid	..	ml	10	10
Quaternary	..	g	1.0	nil
Xylene	..	ml	105	105

over into the condenser despite every care and attention. These two analyses are compared in *Fig. 2*.

The quaternary ammonium compound used in these tests was commercial lauryl pyridinium chloride (*Dehyquart C*) but others were equally as effective. For use, the crystals were dehydrated by heating in oleic acid to 170—180°C at which temperature they dissolved. On cooling, the bulk of the quaternary crystallized out. The viscosity of this slurry was reduced by the addition of about half its volume of xylene. It then proved to be a convenient reagent, allowing the addition of the oleic acid and the anhydrous quaternary compound at the same time.

Discussion

The results presented in *Fig. 1* show that, not only is oleic acid a better reagent than glycerine for reducing the foaming, but also that continuous heating decomposes glycerine with the evolution of water. Since the glycerine had been heated until the liquid temperature had been constant for five minutes (279°C at 630 mm) this additional water must have come from the pyrolysis of the glycerine and/or the shampoo components. That the glycerine was at least partly responsible was confirmed by the odour of acrolein from the black glycerine syrup left in the flask.

When the oleic acid alone gave adequate control of the distillation, the use of the quaternary ammonium compound gave but little benefit (*Fig. 1*). When the oleic acid alone gave insufficient control of the foam, the precipitation of part of the anionic detergent by the quaternary ammonium compound gave excellent control (*Fig. 2*).

Conclusion

The addition of an anhydrous quaternary ammonium compound has been shown to control the foaming of shampoos during distillation and thus allows more rapid and trouble-free determination of the water content.

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