particles of fat, the greater the surface area afforded for contact with oxygen.

Further studies are in progress to gain a better insight into the reasons for the differences between the oxidation rates of the various emulsions, also to evaluate the influence of pro- and antioxidants on the rate of oxidation.

### Summary

The rate of oxidation of various emulsions designed for intravenous use was studied manometrically. Soybean phosphatide dispersions rapidly absorbed oxygen at 38°C. whereas when used in emulsions containing fat with or without additional stabilizing agents, little oxygen was absorbed even when such unsaturated oils as linseed were used. On the other hand, emulsions of oils stabilized with gelatin took up oxygen rapidly, and the finer the size of the fat particles, the more rapidly was oxygen taken up. At 60°C. all rates of oxidation were increased, but the differences between preparations remained. The results are discussed.

REFERENCES

1. Geyer, R. P., Mann, G. V., and Stare, F. J., J. Lab. Clin. Med., *33*, 153–180 (1948).
2. Geyer, R. P., Olsen, F. R., Andrus, S. B., Waddell, W. R., and Stare, F. J., J. Lab. Clin. Med., in press.
3. Shafiroff, B. G. P., and Mulholland, J. H., Ann. Surg., *133*, 145-152 (1951).
4. Meng, H. C., and Freeman, S., J. Lab. Clin. Med., *33*, 689-707 (1948).
5. Holman, R. T., in Holman, R. T., Lundberg, W. D., and Malkin, T., "Progress in the Chemistry of Fats and Other Lipids," vol. 2, p. 85, New York, Academic Press Inc., 1954.
6. Jány, J., Z. angew. Chem., *44*, 348–351 (1931).
7. Johnston, W. R., and Frey, C. N., Ind. Engin. Chem., Anal. Ed., *13*, 479–481 (1941).
8. Nagy, J. J., Vibrans, F. C., and Kraybill, H. R., Oil & Soap, *22*, 349–352 (1944).
9. Umbreit, W. W., Burris, R. H., and Stauffer, J. F., "Manometric Techniques and Tissue Metabolism," 6th ed., Minneapolis, Burgess Publishing Company, 1951.
10. Dutton, H. J., Schwab, A. W., Moser, H. A., and Cowan, J. C., J. Am. Oil Chemists' Soc., *26*, 441–444 (1949).

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# Effect of Inert Atmosphere in the Determination of Free Fatty Acid or Free Caustic Alkali and Unsaponified Material in Soap

E. W. BLANK and E. EMENDORFER, Colgate-Palmolive Company, Jersey City, New Jersey

It has long been recommended in the determination of the free caustic alkali content of soap and soap products that exposure of the alcohol solution of the sample to atmospheric carbon dioxide should be avoided (2, 4, 5, 6). The precaution stems from the observation that alcohol neutralized to a phenolphthalein endpoint (pink) decolorizes almost instantly when shaken or filtered in contact with the atmosphere due to the absorption of carbon dioxide. The absorption of carbon dioxide by alcohol is appreciable, being approximately 2.5 times as great in alcohol as in water under comparable conditions of temperature and pressure (3). Based on this characteristic of neutral alcohol, low results are to be anticipated in the determination of free caustic alkali unless suitable precautions are taken to work in an inert atmosphere. This is not a simple operation and is usually disregarded save for the use of watch glasses to cover beakers and funnels. No estimate of the magnitude of error involved is to be found in the literature.

During the course of investigational work in this laboratory an apparatus of the dimensions and form shown in Figure I was designed. It was subsequently conceived that this apparatus could be adapted to the determination of both free acid or free caustic alkali and unsaponified material in an inert atmosphere.

### Experimental

The apparatus is employed in the following manner. Accurately weigh about 5 g. of the soap sample into the 250-ml. double-necked flask. Pass a slow stream of nitrogen through the flask *via* the small side neck. Add 100 ml. of hot, neutralized alcohol (95% strength or better). Attach the sintered glass filtering unit and flask and, while continuing the flow of nitrogen, place the apparatus on a hot plate. Swirl the contents of the flask occasionally to hasten solution of the sample.

When the sample is in solution, except for alcohol-insoluble salts, remove the flask from the hot plate. Slowly rotate the apparatus to an inverted position so that the alcohol solution in the lower flask filters through the sintered glass filter into the saponification flask without coming in contact with the nitrogen

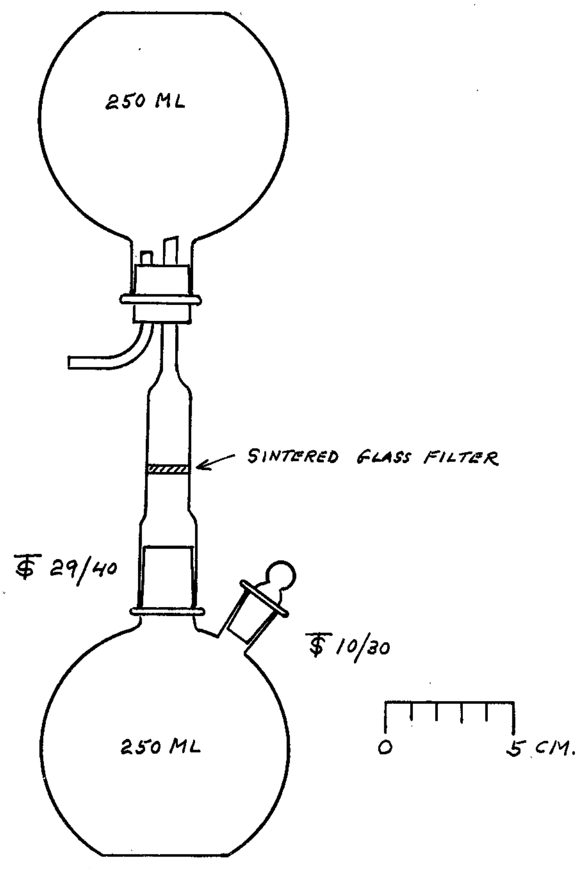

Fig. 1. Apparatus employed to provide an inert atmosphere in the determination of free fatty acid or free caustic alkali and unsaponified material in soap.

inlet in the side neck. Continue the flow of nitrogen throughout this operation. Filtration, aided by the pressure of the nitrogen (caution: employ a pressure safety valve) usually requires 2 to 3 min. or less. Disconnect the saponification flask and close loosely with a stopper bearing a Bunsen valve. By repeating the operation the apparatus can be washed with a small volume of alcohol, but the drainage loss is negligible in view of the total volume of solution and small titration. No change in the final result is usually detectable by washing the flask. Heat the contents of the saponification flask to boiling, remove the stopper, add 4 drops of phenolphthalein indicator (1% in 95% alcohol), and titrate rapidly with either N/10 HCl or N/10 NaOH, depending upon the acidity or basicity of the solution. Calculate, respectively, to free fatty acid or free caustic alkali as percentage $Na_2O$.

Add 5 ml. of N/2 alcoholic NaOH solution, attach to a reflux condenser, and boil gently for 1 hr. Pass nitrogen slowly into the top of the condenser while refluxing. Disconnect the flask from the condenser and allow the solution to cool partially, protecting the contents of the flask with an absorption tube filled with Caroxite. While still warm, back-titrate with N/5 HCl and calculate to unsaponified as percentage $Na_2O$. A blank should be run with each set of samples.

## Results

The results obtained by prescribed use of the apparatus are presented in Table I and II.

## Discussion

The first column in Table I presents the results obtained for free acid and unsaponified material on a lather shave cream employing ordinary laboratory glassware and taking no precautions against carbon dioxide absorption beyond keeping the alcohol hot throughout the duration of the determination and working as rapidly as possible. The alcoholic solution of the sample did not require filtration after the titration for free fatty acid and prior to the saponification step since the amount of alcohol-insoluble matter present was so small it could be disregarded. The second column of Table I presents the results obtained by working in a nitrogen atmosphere, using the apparatus described previously. The acidity was found to be the same under both conditions of determination. The unsaponified values demonstrate a greater scatter (non-significant statistically) when determined by the usual laboratory procedure.

TABLE I

Free Acidity and Unsaponified in Lather Shave Cream

| I One hour saponification. No protection against atmospheric $CO_2$ | | II One hour saponification. Nitrogen atmosphere | |
|---|---|---|---|
| Acidity as $Na_2O$ | Unsaponified as $Na_2O$ | Acidity as $Na_2O$ | Unsaponified as $Na_2O$ |
| 0.36 | 0.17 | 0.37 | 0.18 |
| 0.36 | 0.18 | 0.38 | 0.19 |
| 0.38 | 0.19 | 0.38 | 0.18 |
| 0.37 | 0.18 | 0.37 | 0.19 |
| 0.38 | 0.19 | 0.37 | 0.19 |
| 0.38 | 0.18 | 0.37 | 0.19 |
| 0.39 | 0.19 | 0.37 | 0.18 |
| 0.37 | 0.17 | 0.38 | 0.19 |
| 0.37 | 0.19 | 0.38 | 0.18 |
| 0.37 | 0.18 | 0.37 | 0.18 |

The results shown in Table II for free caustic alkali and unsaponified material in a sprayed, filled soap are of greater value in demonstrating the differences resulting from working under the usual laboratory conditions as contrasted with working in an inert atmosphere. Under the latter conditions higher values are obtained for the free caustic alkali content. Conversely the values for unsaponified material show a decrease. This is due to the fact that if carbon dioxide is absorbed during the saponification, only one-half of the sodium carbonate formed by carbonation is titrated during the back-titration to phenolphthalein indicator, thus yielding high results for the unsaponified determination.

TABLE II

Free Caustic Alkali and Unsaponified Material in a Sprayed, Filled Soap

| I One hour saponification. No protection against atmospheric $CO_2$ | | II One hour saponification. Nitrogen atmosphere | |
|---|---|---|---|
| Free caustic as $Na_2O$ | Unsaponified as $Na_2O$ | Free caustic as $Na_2O$ | Unsaponified as $Na_2O$ |
| 0.007 | 0.067 | 0.013 | 0.030 |
| 0.010 | 0.061 | 0.017 | 0.048 |
| 0.007 | 0.061 | 0.010 | 0.049 |
| 0.010 | 0.085 | 0.017 | 0.042 |
| Nil | 0.079 | 0.014 | 0.049 |
| Nil | 0.067 | 0.010 | 0.067 |
| Nil | 0.067 | 0.010 | 0.061 |
| Nil | 0.055 | 0.007 | 0.061 |

Work analogous to that presented in Table II, employing spray-filled soaps containing free caustic alkali content of 0.01 to 0.06% free caustic and amounts of unsaponified material ranging as high as 0.16% gave similar results.

It should be pointed out, as general information, that if a soap contains a high concentration of free caustic alkali together with unsaponified material, the above method of determination is open to criticism on the grounds that during heating with alcohol the free alkali will saponify a chemically equivalent amount of the unsaponified material. In such a case Devine's method is available (1). It has been the experience of this laboratory that amounts of free caustic alkali of 0.1% $Na_2O$ or less do not react in this manner.

## Conclusions

The conclusions to be drawn from this work can be summarized as follows:

a) Values for free fatty acid are not significantly affected by carbonation when run under the usual laboratory conditions. Under similar conditions free caustic alkali values are low (statistically significant) and, conversely, unsaponified values are high (statistically significant).

b) The magnitude of the error incurred by working under the usual laboratory conditions is so small as to be negligible unless extreme precision is required.

c) Hot alcohol apparently provides its own protective vapor barrier preventing carbon dioxide absorption. This characteristic of alcohol can be further enhanced by the judicious use of watch glasses to cover beakers and funnels during the determination.

REFERENCES

1. Devine, R. E., J. Am. Chem. Soc., *22*, 693 (1900).
2. Federal Specification P-S-536b (1951), Method 30.1.1 and 30.2.2.
3. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," vol. 6, pp. 48 and 54, Longmans, Green, and Company, New York (1945).
4. Official and Tentative Methods of the American Oil Chemists' Society, Official Method Da 4a-48 (1954).
5. Scott, "Standard Methods of Chemical Analysis," 5th ed., vol. 2, p. 2033, D. Van Nostrand Company Inc., New York (1939).
6. Subcommittee on Methods of Soap Analysis, Report No. 3, Analyst, *62*, 36 (1937).

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