The Chemical Determination of the Tocopherols in Distilled Concentrates*

H. W. RAWLINGS

THE method (1) of Emmerie and Engel for estimating tocopherol with ferric chloride and alpha, alpha'-dipyridyl has been modified by carrying out the reactions in the absence of light and by using hydroquinone as a basic standard.

The procedure is as follows:

Solutions:
- (a) Ferric chloride (hydrated) 0.10% in absolute ethanol. (Solution must be stored in an opaque bottle.)
- (b) Alpha, alpha'-dipyridyl (Eastman Kodak Company) 0.25% in absolute ethanol. (Solution must be stored in an opaque bottle.)

Solvent: Absolute ethanol distilled from KOH and $KMnO_4$.

Apparatus: Photoelectric colorimeter (Evelyn) (2) equipped with a filter with maximum transmission at 520 mmu.

A weighed sample of vitamin E-bearing material is transferred to a volumetric flask with absolute ethanol. Dilutions are made such that a 1 ml. aliquot of the final solution will contain from 0.00005 to 0.0003 gm. of tocopherol. One milliliter of this solution is transferred to a 2-ounce opaque bottle, and 1 ml. of the ferric chloride solution and 1 ml. of the alpha, alpha'-dipyridyl solution are added. Sufficient redistilled absolute ethanol is now added to bring the total volume up to 25 ml. The bottle is closed with a glass stopper, and the reaction is allowed to proceed (at normal room temperature) for ten minutes from the time of the addition of the ferric chloride.

A blank is prepared at the same time, consisting of 1 ml. of the ferric chloride solution, 1 ml. of the alpha, alpha'-dipyridyl solution and 23 ml. of alcohol. After this has stood for ten minutes, it is quickly transferred to the colorimeter which is then adjusted for 100% transmission (0.0 absorption) with the 520 mmu filter. The blank is removed from the instrument and the sample solution is quickly poured into a test tube already placed in the colorimeter. The reading (G) of the galvanometer gives the tocopherol content of the aliquot by means of a calibration chart made with pure tocopherol or hydroquinone.

In the presence of light, the ferric chloride will oxidize the ethanol giving a spurious color formation. The opaque bottle has been found to be a sufficient protection, and its use is considerably more convenient than working in a darkened room.

The reaction is substantially complete in one minute, but the analyses of concentrated preparations of tocopherol are somewhat more precise if a ten minute period is used. (If preparations containing oxidizable impurities are used, the one minute reading may be the more reliable.)

THE colored product formed by the combination of the alpha, alpha'-dipyridyl and the ferrous iron has a broad absorption maximum at 520 mmu. Therefore, using a filter with a narrow maximum absorption at 520 mmu, the laws of Beer and Lambert should prevail substantially over the recommended range of the instrument. From the formula,

$$L = 2\text{-}\log_{10}G,$$

is obtained a property "L" which is analogous to the optical density as used in spectroscopy. A graph may be prepared using "L" as ordinate and percent tocopherol as abscissa; or a straight line relation between "G" (the galvanometer reading) and tocopherol may be plotted using 2 cycle logarithm paper (See Fig. 1).

Theoretically, hydroquinone is equivalent to tocopherol for the reduction of ferric chloride to ferrous chloride and therefore may be used to prepare a base chart for determining tocopherol. This is shown experimentally using the pure tocopherols by the data illustrated in Figure 1.

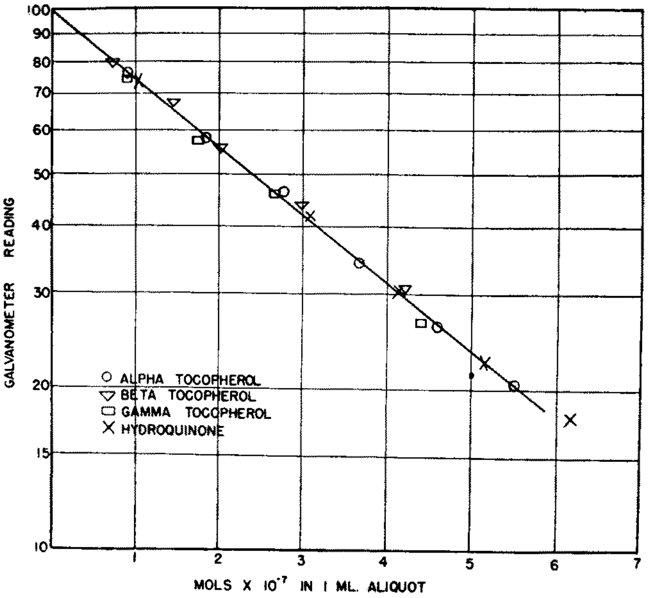

FIG. 1.

This figure shows points obtained by plotting the galvanometer reading against moles of reducing agent present in the aliquot. (The molecular weights of alpha-tocopherol, of beta- and gamma-tocopherol, and of hydroquinone are 430, 416 and 110, respectively.) The line determined by the points of the hydroquinone data coincides satisfactorily with the points for the tocopherols. It is therefore apparent that hydroquinone is a suitable standard for the determination of tocopherol by this method.

The use of a type of colorimeter other than the Evelyn should be readily worked out by a chemist familiar with colorimetry.

The above procedure for the determination of tocopherol has been used for factory control analysis of distilled concentrates of natural tocopherols containing from 15% to 80% tocopherols. Many other products containing as little as 0.5% tocopherols may be

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directly assayed by this method, but it should be kept in mind that the Emmerie and Engel reaction measures total reducing power. Therefore, other reducing substances, including carotenoids, will give false readings for tocopherol, and the method should not be applied to crude materials.

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Continuous Lithium and Aluminum Stearate Grease Manufacture

H. G. HOULTON, B. D. MILLER, P. A. LENTON, J. A. TAYLOR, and B. E. ADAMS
The Girdler Corporation, Louisville, Kentucky

THE Votator has been used extensively in the commercial manufacture of margarine, shortening and lard. More recently it has found commercial application in the manufacture of soap, crystallization of paraffin wax, pasteurization and freezing of eggs. To this list can now be added the continuous manufacture of aluminum and lithium stearate lubricating greases.

The batch method of manufacturing lithium and aluminum greases consists in heating the soap and oil to the dissolving point in an open kettle. The hot grease is then run into small pans to cool and gel. These pans hold about 35 to 50 pounds. The cooling rate is generally controlled and takes about twelve hours. The cooled grease is then transferred from the pans to some type of hopper where the grease is picked up by a pump for working the grease to a fairly constant consistency and then pumped to containers for shipment. Over-all rates of production for this batch method vary about 1,000 to 2,000 pounds per hour and this necessitates considerable handling and transferring of the grease.

In the case of lithium grease a light oil of about 300° F. flash point is used and, since the slurry needs to be heated to about 400° F. to completely dissolve the soap, this introduces a fire hazard. A completely enclosed, continuous process, therefore, provides safety, eliminates handling and transferring and provides a much closer control of operational variables.

Equipment and Operation

The continuous process for lubricating greases herein reported was carried out on a pilot plant scale at rates varying from about 30 pounds per hour to 200 pounds per hour.

Three-inch diameter Votators, equipped with a 2¼-inch diameter shaft and two stainless blades, were used. The assembly of one of these units is given in Figure 1. Cooling units were helically jacketed while the Dowtherm unit had an open jacket in order to secure low jacket pressure drops. A flow sheet of the process as finally developed is given in Figure 2.

An oil and soap slurry was placed in a slurry tank, as indicated in the flow sheet. With certain oils the slurry picked up air from the atmosphere and this slurry was, therefore, passed to a deaerator where this air was removed. The deaerated slurry was then passed to a heating Votator where the slurry was simultaneously mixed and heated to a point where the soap dissolved completely. This required temperatures in the range of 300° F. for aluminum greases and in the range of 400° F. for lithium greases.

The hot grease was then immediately cooled to a pre-determined critical value in the second Votator, and passed through a gelling section sufficiently large to allow the grease to set. This was followed by a third Votator in series where the grease structure was broken down to nearly the maximum capacity. That is, the grease leaving this unit was such, that further working changed its consistency only slightly.

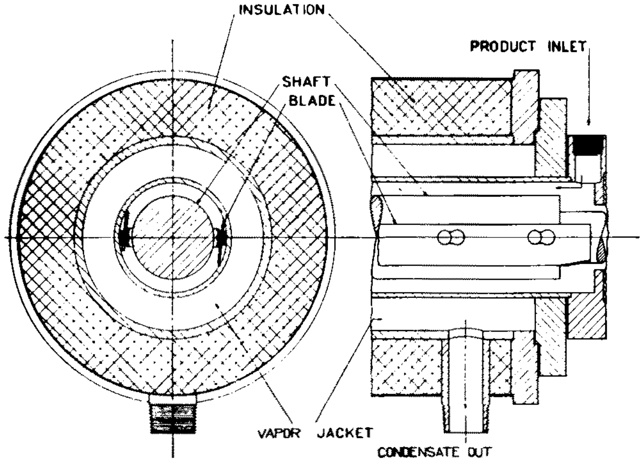

FIG. 1. Longitudinal and cross sectional view of pilot plant votator.

Variables studied included the following: (a) Grease formulation was studied in which not only the types of oils used were examined, but also the quantity of materials blended, the type of soap to give the best yields and the amount of mixing necessary to produce a fairly uniform slurry. (b) The type and design of proper evacuation equipment was studied. (c) The critical temperatures, pressures, blade velocities, through-put rates, retention times and overall heat transfer coefficients for each of the three Votators used were determined. (d) The temperature, holding times and proper design of gelling section were established. (e) The design and critical conditions necessary for the working Votator were developed.

These variations led to a wide number of combinations and permutations but have in general been quite widely covered for the manufacture of lithium and aluminum greases.