# Pinitol and Quebrachitol Esters of Linseed Fatty Acids[*][1]

A. E. RHEINECK and R. M. BRICE, Archer-Daniels-Midland Company,
Research Laboratory, Minneapolis, Minnesota

THE drying properties of fatty acid esters of the cyclic polyols, inositol, quebrachitol, and pinitol, have been investigated only to a very limited extent. Van Alphen (1) prepared linseed esters of quebrachitol, and Bolley (2) investigated inositol esters. Gibbons and Gordon (3) prepared varnishes from inositol-linseed fatty acid esters without studying the film properties of the intermediate oils. No literature references to drying oil esters of pinitol were found.

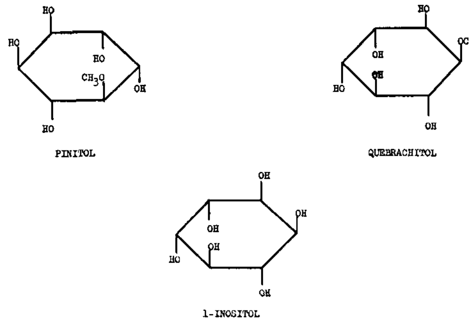
As part of a program of investigation of the properties and uses of esters prepared from various polyols, it seemed timely to investigate oils which might be obtained when the cyclitols, pinitol, and quebrachitol were esterified with linseed fatty acids. For comparative purposes, similar esters of mono-, di-, and tri-pentaerythritol, glycerol, erythritol, and inositol were prepared and evaluated.

The quebrachitol used in this work was obtained from the rubber latex serum. Methods for recovery of this cyclitol are described by Van Alphen (1) and by Hart (5).

Recently Anderson (4) reported his investigation of the recovery of pinitol from western sugar pine stumps. He prepared only such derivatives of pinitol as were necessary to identify its structure.

Pinitol and quebrachitol are isomeric derivatives of inositol, pinitol being the mono-ethyl ether of a d-inositol and quebrachitol being the mono-methyl ether of l-inositol. The structures of these three cyclitols as proposed by Angyal and MacDonald (6) are shown in Figure 1.

FIG. 1. Configurations of cyclitols.



J. Angyal and G. G. MacDonald, J. Chem. Soc. 1952, 686-95

Preliminary work with quebrachitol was carried out on material obtained directly from Malaya.[2] This product yielded linseed esters which were darker than a Gardner color of 18. They dried to good hard films with unusual depth of gloss. More recent lots[3] of this polyol, when esterified, showed only a slight improvement in ester color.

The pinitol[4] as received, yielded a linseed ester with a Gardner color of 7. This was considered satisfactory. The meso form of inositol[5] was used in this work. It was a purified product considered satisfactory without further treatment.

BECAUSE of the unsatisfactory color of the quebrachitol esters, methods were studied for purification of this cyclitol. A modification of the method described by Anderson (4) was employed. An aqueous solution of quebrachitol was treated with barium hydroxide to precipitate gums. Excess barium ions were removed by treatment with carbon dioxide followed by filtration. The filtrate was evaporated to a thick syrup from which the quebrachitol was precipitated by the addition of glacial acetic acid. The crystallized product was filtered, washed with acetic acid, and dried. As shown in Table I, this process raised the melting point from the 177-182°C. range to a range of 185-188°C. and increased the hydroxyl content from 41.3% to 42.7%. The theoretical value is 43.8%. This product when esterified with linseed acids yielded an ester with a Gardner color of 5.

TABLE I
Analytical Constants of Polyols

| Polyol | | Per cent hydroxyl | | Melting point °C. |
|---|---|---|---|---|
| Name | Type | Found | Theoretical | |
| Quebrachitol[a] | Crude | 41.3 | ...... | 172-182 |
| Quebrachitol | Purified | 42.7 | 43.8 | 185-188 |
| Pinitol[b] | As received | 42.8 | 43.8 | 176-185 |
| Inositol[c] | As received | 56.6 | 56.6 | 225-227 |
| Mono-pentaerythritol | As received | 49.8 | 50.0 | ...... |
| Di-pentaerythritol | As received | 39.7 | ...... | ...... |
| Tri-pentaerythritol | As received | 35.1 | ...... | ...... |
| Erythritol | As received | 54.9 | 55.7 | ...... |

[a] Obtained from U. S. Rubber Co. Plantation Division.
[b] Obtained from Dr. A. B. Anderson, University of California.
[c] Obtained from A. E. Staley Co.

The physical and chemical properties of all of the polyols used in this work are shown in Table I. The water-white linseed acids had an acid value of 200 and iodine value of 184.

All of the oils used in this work were prepared by the azeotropic reflux method, using xylene as the azeotrope at a temperature of 235-240°C. A three-necked, 1-liter flask, equipped with a Barrett trap, stirrer, thermometer, and inert gas inlet tube, was used. Carbon dioxide was bubbled through the system during the entire process at the rate of 2.8 liters per hour.

In the esterification of the cyclitols, the molar ratio of fatty acids to polyols was varied. In esterifications involving inositol, the ratios of fatty acids to polyol were respectively 6, 5, and 4 to 1. For pinitol and quebrachitol, ratios of 5, 4, and 3 to 1 were used. In the control esterifications, equivalent quantities of fatty acids and polyols were employed.

Esterification catalysts were omitted in this work in order to eliminate the additional variable factor which would be introduced.

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[*] Presented at the 27th fall meeting of the American Oil Chemists' Society in Chicago, Nov. 2-5, 1953.
[1] Technical Paper No. 126.
[2] Malayan American Plantation, Ltd., Penang, Malaya.
[3] Obtained from U. S. Rubber Co. Plantation Division, New York, N. Y.
[4] Dr. A. B. Anderson, University of California, Berkeley, Calif.
[5] A. E. Staley Company, Decatur, Ill.

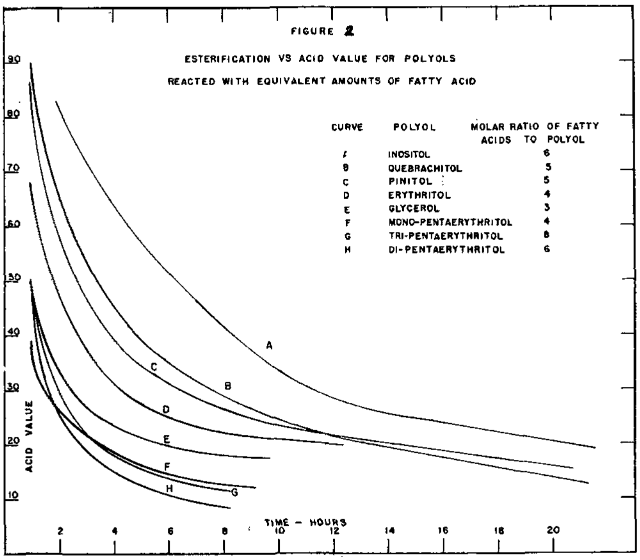
FIGURE 2
ESTERIFICATION VS ACID VALUE FOR POLYOLS REACTED WITH EQUIVALENT AMOUNTS OF FATTY ACID

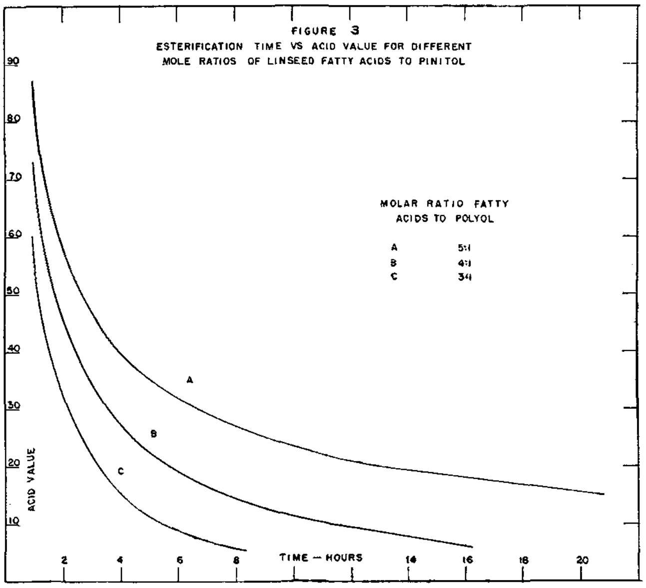
FIGURE 3
ESTERIFICATION TIME VS ACID VALUE FOR DIFFERENT MOLE RATIOS OF LINSEED FATTY ACIDS TO PINITOL

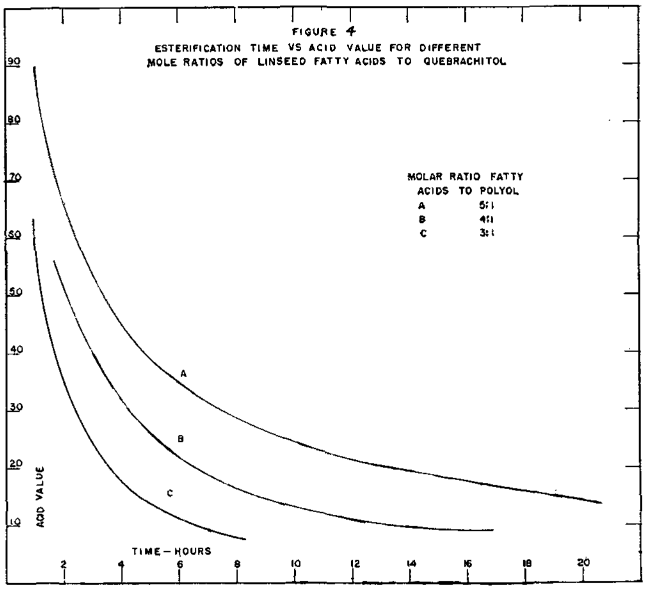
FIGURE 4
ESTERIFICATION TIME VS ACID VALUE FOR DIFFERENT MOLE RATIOS OF LINSEED FATTY ACIDS TO QUEBRACHITOL

After esterification was considered complete, as indicated by the leveling off of the acid value *versus* time curves, the esters were "topped." Volatile products and free fatty acids were removed by heating to a maximum temperature of 235°C. at 0.5 mm. of mercury pressure for 30 minutes. Figures 2, 3, and 4 are esterification curves for the esters prepared in this study. Esterification of the cyclitols was considered essentially complete at about 21 hours, as compared to approximately 8 hours for the several pentaerythritols (*cf.* Fig. 2). The time required for the erythritol ester was about 12 hours. Esters of the three cyclitols, glycerol, and erythritol had considerably higher final acid values than did the several pentaerythritol esters, namely a range of 14-20 as compared with a range of 8-12.

FROM the curves of Figure 2 it is obvious that the cyclitols, glycerol, and erythritol are more difficult to esterify than the pentaerythritols when equivalent quantities of fatty acids and polyol are used. The curves indicate that these variations in esterification rates are influenced by type of hydroxyl groups—whether primary or secondary. Erythritol, having 2 secondary and 2 primary hydroxyl groups, esterifies at a rate intermediate to that of the cyclitols, having only secondary hydroxyl groups, and the pentaerythritols, having only primary hydroxyl groups. Glycerol, having 2 primary and 1 secondary hydroxyl, esterifies at a rate intermediate to erythritol and the pentaerythritols. The variations in esterification rates, as shown by the curves of Figure 2, indicate that the rates for pinitol and quebrachitol seem to be influenced chiefly by the character of the secondary hydroxyl groups rather than by their cyclic structure.

When the theoretical molar ratios of fatty acids and cyclitols were used, the rate of esterification of inositol was slower than that of the pinitol and quebrachitol, as shown by curves A, B, and C of Figure 2. This is contrary to the expectation that the esterification rates for the three cyclitols would be the same. This difference in rate may be caused by variations in solubility of the cyclitols as indicated by visual observations. The esterification mixtures of pinitol or quebrachitol with fatty acids are homogeneous at reaction temperatures whereas the inositol reaction mixture forms a two-phase system. It appears that the presence of a methoxy group in the former cyclitols is sufficient to improve their solubility in the fatty acids and hence increase the esterification rate. The esterification curves for the pinitol and quebrachitol esters (curves B and C of Figure 2 and curves A, B, and C of Figures 3 and 4) are practically identical, as might be anticipated from the similarity of their structures. The esterification curves for pinitol and quebrachitol at different molar ratios of fatty acids to cyclitol are shown in Figures 3 and 4, respectively. The expected results, namely, increased esterification rates, were obtained when the molar ratio of fatty acid to cyclitol was reduced from 5 to 1 to 3 to 1. Pinitol, for example, at a ratio of 5 to 1 was esterified to an acid value of 15.5 in 20 hours and at a ratio of 4 to 1 esterified to a lower acid value, *i.e.*, 6.5, in the shorter time of 16.5 hours.

A similar series of inositol esters was prepared with mole ratios of fatty acids to cyclitol varying from 6 to 1 down to 4 to 1. Erratic results were obtained when 5 to 1 and 4 to 1 ratios were used. A

TABLE II

Characteristics of Linseed Fatty-Polyol Esters

| Ester composition | | Final analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Polyol | Moles fatty acid per mole polyol | Acid value | Viscosity (Stokes) | Color (G) | Saponification value | Per cent hydroxyl | Specific gravity | Iodine value | |
| | | | | | | | | Determined* | Corrected |
| Inositol | 6 | 9.1 | 4.6 | 5-6 | 191.8 | 0.85 | 0.9471 | 164.0 | 171.1 |
| Inositol | 5 | 7.6 | 5.1 | 4-5 | 189.7 | 0.74 | 0.9481 | 163.3 | 170.5 |
| Inositol | 4 | 3.1 | 6.2 | 4-5 | 185.0 | 1.21 | 0.9519 | 163.6 | 177.0 |
| Pinitol | 5 | 6.1 | 2.5 | 4-5 | 186.9 | 0.49 | 0.9494 | 158.8 | 170.0 |
| Pinitol | 4 | 5.6 | 2.7 | 7-8 | 182.9 | 1.25 | 0.9555 | 159.1 | 174.2 |
| Pinitol | 3 | 4.8 | 5.4 | 9-10 | 174.5 | 3.08 | 0.9702 | 155.3 | 178.0 |
| Quebrachitol | 5 | 8.5 | 2.8 | 3-4 | 185.0 | 0.81 | 0.9501 | 160.0 | 173.0 |
| Quebrachitol | 4 | 6.5 | 4.2 | 4-5 | 180.7 | 1.89 | 0.9577 | 158.5 | 175.5 |
| Quebrachitol | 3 | 5.6 | 10.2 | 5 | 172.7 | 3.80 | 0.9718 | 153.6 | 178.0 |
| Pure pentaerythritol | 4 | 4.9 | 1.2 | 3-4 | 189.9 | 0.73 | 0.9337 | 170.0 | 179.2 |
| Di-pentaerythritol | 6 | 7.3 | 1.4 | 5 | 185.4 | 0.57 | 0.9385 | 165.2 | 178.2 |
| Tri-pentaerythritol | 8 | 4.5 | 2.2 | 5-6 | 182.2 | 0.44 | 0.9477 | 162.1 | 178.0 |
| Glycerol | 3 | 9.5 | 0.5 | 3-4 | 192.2 | 0.54 | 0.9270 | 171.5 | 178.5 |
| Erythritol | 4 | 5.0 | 1.4 | 5-6 | 189.8 | 0.27 | 0.9355 | 166.6 | 175.0 |

For esterification time and acid values see Figures 2, 3, and 4. * Wijs.

considerable quantity of an oil-insoluble, crystallizable substance separated from the reaction mixture. This material had a hydroxyl content of 35% compared with the theoretical value of 56.6% for inositol. Further identification of the compound was not undertaken, but it probably is unreacted inositol, as previously indicated in esterification studies by Gibbons and Gordon (3).

The data on saponification and hydroxyl values (8) shown in Table II also indicate that, regardless of the excess inositol charged, these constants are quite comparable. This tends to verify (3) a conclusion that the final product is largely the hexa-ester regardless of the ratio of fatty acids to inositol charged. The partial ester content is appreciably lower than in the cases of pinitol and quebrachitol, as indicated by the range of saponification and hydroxyl values.

The physical and chemical properties of all unbodied esters are shown in Table II. The method of preparation was comparable for all of these esters; however it is not considered optimum for the inositol series because of the previously mentioned sludge separation.

The colors of the several inositol esters were constant, that is, about 4-6 Gardner. The colors of the pinitol and quebrachitol ester show a darkening trend as the molar ratio of fatty acids to cyclitol decreases.

IODINE values (Wijs) of the esters as measured were corrected for differences in molecular weights of the polyols and for differences in the degree of esterification. The corrected iodine value [6] (based on determined saponification and iodine values) therefore indicates the true unsaturation in only the fatty acid residues of the esters.

The corrected iodine values for the cyclitols at the higher molar ratios of fatty acids to polyol are a little lower than for the control esters. The former were 170-173 and the latter 178-179, excepting the erythritol ester which had a corresponding value of 175. This is probably caused by the difference in the amount of polymerization resulting from the longer processing at high temperature during the esterification of the former, *i.e.*, 21 hours *versus* 8 hours. The time for the erythritol ester was intermediate at 12 hours. The small amount of polymerization as measured by a loss of 6-8 iodine value units is insufficient to have any appreciable effect on the viscosity of the esters in the range below 7.5 stokes. This was verified from data obtained by studying the effect of heat-bodying of several esters. Table III shows the relationship between corrected iodine value and viscosity for several esters during the early stages of heat-bodying. The maximum change in viscosity is 1.1 stokes for a 10-unit drop in iodine value in the range below 7.5 stokes.

TABLE III

Variation of Viscosity With Iodine Value While Heat Bodying

| Polyol | Molar ratio fatty acids to polyol | Viscosity* in Stokes at different iodine values | | Viscosity increase (Stokes) with 10 unit drop in corrected iodine value |
|---|---|---|---|---|
| | | Corrected I.V. 170 | Corrected I.V. 160 | |
| Pinitol | 5 | 2.5 | 2.7 | 0.2 |
| Pinitol | 4 | 2.8 | 3.4 | 0.6 |
| Quebrachitol | 5 | 3.0 | 3.4 | 0.4 |
| Inositol | 6 | 4.7 | 5.8 | 1.1 |
| Mono-pentaerythritol | 4 | 1.8 | 2.3 | 0.5 |

* Based on curve plotted from data obtained from samples taken while heat bodying.

An inspection of the viscosity data on unbodied esters given in Table II indicates a higher initial viscosity for all of the cyclitol esters as compared to the various non-cyclic control esters. As an example, a 6 to 1 molar ratio inositol ester had a viscosity of 4.6 stokes and an 8 to 1 tripentaerythritol ester had a viscosity of 2.2 stokes. Hence it appears that either the cyclic structure or the secondary hydroxyl groups are responsible for the higher viscosities of the cyclitol esters.

In the inositol, pinitol, and quebrachitol series of esters, viscosity is related to the degree of esterification. The completely esterified product in any series has the lowest viscosity. Viscosity increases with the hydoxyl content. The hydroxyl content of the cyclitol esters increases with decreases in the molar ratios of fatty acids to polyol. This is as anticipated (*cf.* Table II).

When the viscosities of the completely esterified cyclitols are considered, the pinitol and quebrachitol

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[6] Corrected iodine value $= \frac{56.1 \times 1{,}000}{\text{Sap. value} \times 280} \times$ iodine value (actual) $=$ $\frac{\text{Equivalent weight}}{280} \times$ I.V. (actual).

TABLE IV

Characteristics of Heat Bodied Linseed Fatty Acid Polyol Esters

| Ester composition | | Overall time to $Z_2$ visc. (hours) | Rate in range U-$Z_2$ (Stokes per hour) | Acid value | Saponification value | Per cent hydroxyl | Viscosity Stokes | Iodine value | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Polyol | Moles fatty acid per mole polyol | | | | | | | Determined* | Corrected | Drop in corrected |
| Inositol | 6 | 2.0 | 13.8 | 5.2 | 190.0 | 0.7 | 38.0 | 146.5 | 154.2 | 16.9 |
| Inositol | 5 | 1.75 | 13.8 | 3.7 | 188.6 | 0.6 | 37.7 | 144.9 | 154.0 | 16.5 |
| Inositol | 4 | 1.75 | 13.8 | 2.0 | 187.6 | .... | 35.0 | 148.1 | 158.1 | 18.9 |
| Pinitol | 5 | 4.0 | 10.1 | 4.6 | 186.2 | 0.3 | 39.4 | 133.0 | 142.9 | 27.1 |
| Pinitol | 4 | 3.9 | 9.2 | 2.8 | 185.2 | 0.8 | 39.4 | 132.7 | 143.0 | 31.2 |
| Pinitol | 3 | 3.1 | 8.9 | 2.8 | 174.0 | 2.0 | 36.2 | 133.0 | 153.0 | 25.0 |
| Quebrachitol | 5 | 4.0 | 10.1 | 6.5 | 183.1 | 0.5 | 40.8 | 134.7 | 146.8 | 26.2 |
| Quebrachitol | 4 | 3.3 | 9.2 | 3.2 | 181.9 | 1.4 | 38.7 | 136.9 | 150.2 | 20.4 |
| Quebrachitol | 3 | .... | ...... | 3.2 | 178.0 | 2.0 | 39.4 | 136.8 | 153.2 | 25.7 |
| Pentaerythritol | 4 | 7.0 | 6.8 | 2.9 | 187.1 | 0.2 | 37.8 | 127.8 | 131.2 | 43.0 |
| Di-pentaerythritol | 6 | 3.4 | 15.1 | 1.6 | 182.8 | 0.3 | 38.0 | 133.6 | 146.2 | 32.0 |
| Tri-pentaerythritol | 8 | 2.3 | 19.8 | 3.9 | 180.3 | 0.3 | 49.7 | 136.5 | 151.3 | 26.7 |
| Erythritol | 4 | 5.9 | 13.6 | 5.9 | 190.3 | 0.2 | 35.8 | 126.2 | 132.8 | 42.8 |

* Wijs.

products are comparable but distinctly lower than the corresponding inositol ester. It is thought that either the higher molecular weight of the inositol esters or the solubilizing effect of the methoxy group in the former esters or both of these factors together produce such viscosity differences.

In the three families of esters—inositol, pinitol, and quebrachitol—the specific gravity increases with the free hydroxyl content. This is in agreement with similarly observed data on partial esters of glycerol and the various pentaerythritols. With the three pentaerythritol esters the specific gravity increases with the molecular size of the alcohol. An inspection of the data in Table II indicates that in virtually all cases the specific gravities of the cyclitol esters are greater than those of the controls. The value for tripentaerythritol is 0.9477, which is about the same as the corresponding value for the completely esterified inositol ester.

The relationship between viscosity and structure of the polyols was further studied by heat-bodying several of the oils from each group. This was achieved by heating the esters to 288°C. at 5 mm. of Hg. pressure until a viscosity of $Z_2$ was reached. The equipment used for these experiments consisted of a three-necked flask fitted with stirrer, thermometer, sampling tube, and vacuum take-off. Samples were periodically removed under vacuum, cooled immediately to 25°C., and checked for viscosity so that the rate of polymerization could be followed.

THE polymerization curves are plotted in Figures 5, 6, 7, and 8 on a semi-logarithmic scale. In these figures zero time was taken when the oil reached 288°C. For comparative purposes the polymerization rates of all of the esters are shown in Table IV. These rates were obtained from Figures 5 through 8. With the exception of curves C and D of Figure 8, representing the erythritol and monopentaerythritol esters, the rates are represented by essentially straight lines throughout the bodying range.

The bodying rates of the esters do not vary with the configuration of the polyol but do change with the number of esterified hydroxyl groups. The rates from fastest to slowest are as follows: tripentaerythritol with 8; dipentaerythritol and inositol, each with 6; pinitol and quebrachitol, each with 5; and finally monopentaerythritol and erythritol, each with 4. Pre-

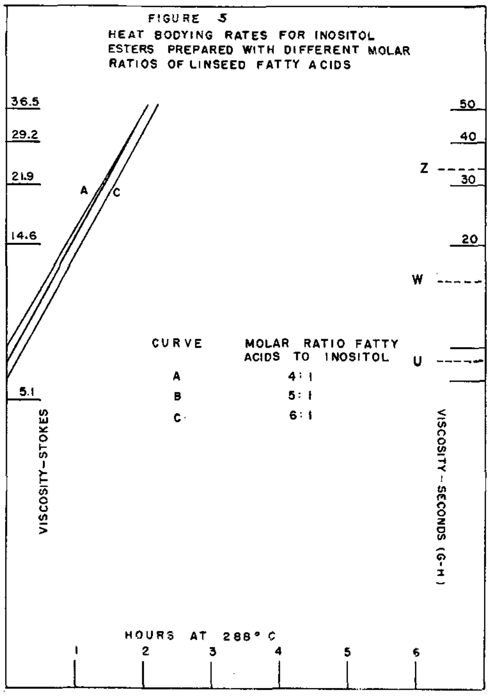
FIGURE 5
HEAT BODYING RATES FOR INOSITOL ESTERS PREPARED WITH DIFFERENT MOLAR RATIOS OF LINSEED FATTY ACIDS

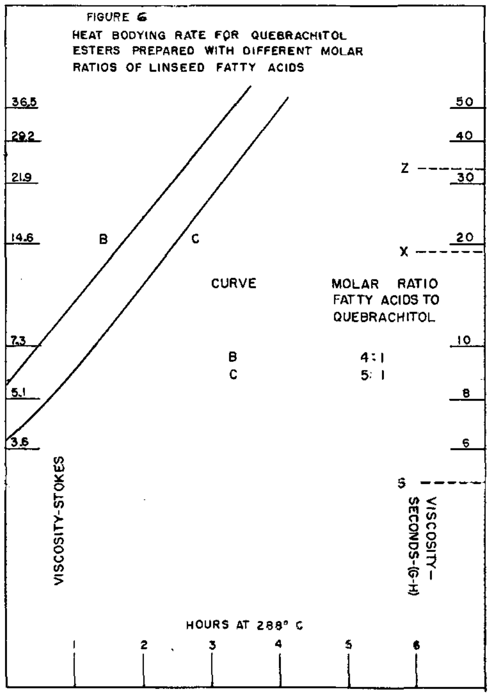
FIGURE 6
HEAT BODYING RATE FOR QUEBRACHITOL ESTERS PREPARED WITH DIFFERENT MOLAR RATIOS OF LINSEED FATTY ACIDS

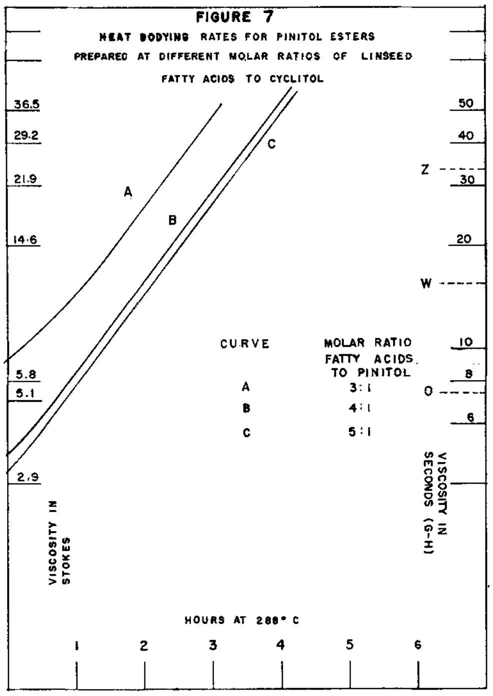
FIGURE 7
HEAT BODYING RATES FOR PINITOL ESTERS PREPARED AT DIFFERENT MOLAR RATIOS OF LINSEED FATTY ACIDS TO CYCLITOL

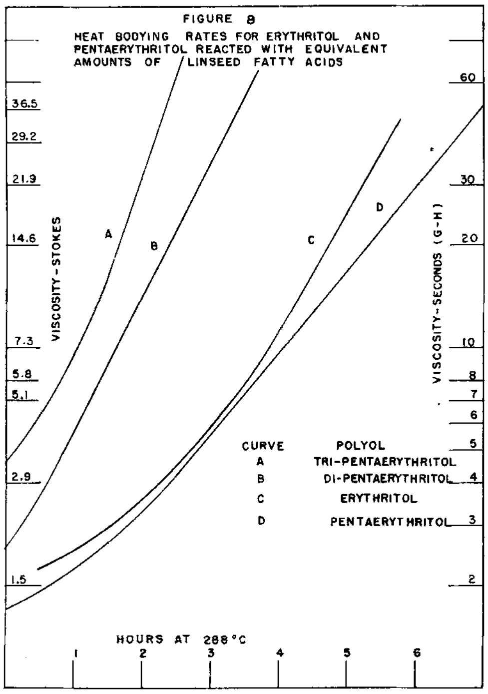
FIGURE 8
HEAT BODYING RATES FOR ERYTHRITOL AND PENTAERYTHRITOL REACTED WITH EQUIVALENT AMOUNTS OF LINSEED FATTY ACIDS

vious work (7) has shown that esters of glycerol with three hydroxyl groups body slower than esters of monopentaerythritol.

The curves for the heat-bodying of the inositol esters prepared using different fatty acid to polyol ratios are shown in Figure 5. They have the same slope, are practically coincident, and have almost the same initial starting viscosity. The latter point helps to verify the observation, previously made, that a hexa ester rather than a penta or tetra ester predominates in the reaction mixture regardless of the ratio of fatty acids to inositol charged.

The heat-bodying curves for the several pinitol and quebrachitol esters at different fatty acid to polyol mole ratios are shown in Figures 6 and 7. The slopes of all these curves are identical for the same fatty acid mole ratio, indicating that bodying rates are equivalent. However the time to reach $Z_2$ viscosity is inversely related to the number of fatty acid chains on the cyclitols. This behavior is apparently caused by the differences in the initial viscosity of these esters.

We have given in Table III the corrected iodine values of the bodied oils and the drop in corrected iodine value during heat bodying. The losses in iodine value for the esters of the same alcohol were comparable. The table also shows the hydroxyl content of the esters before and after bodying. In the cases of the partially esterified pinitol and quebrachitol, polymerization rates are related inversely with the initial hydroxyl values. The initial viscosity as related to the initial hydroxyl content is shown in this table also.

The drop in corrected iodine value (Table IV) is a measure of the degree of polymerization *via* the fatty acid structure. In all the groups of esters the drop is inversely related to the functionality of the polyol. The losses in the esters of the cyclitols are less than those in the pentaerythritols, which point again reflects the higher initial viscosities within the former group.

The drying times of the limpid and bodied esters were determined on a Sanderson drier at 25 ± 1°C. and 50 ± 5% relative humidity. Naphthenate driers were used at the following metal content based on the amount of ester: 0.5% of Pb, 0.05% of Co, 0.025% of Mn, and 0.01% of Ca. The final dry was the point at which the film surface did not show an imprint of the sand particles. These data are shown in Table V.

TABLE V

Drying Properties of Polyol-Linseed Fatty Acid Esters

| Unbodied | | Polyol | Molar ratio fatty acids to polyol | Bodied to $Z_2$ (Gardner) | |
|---|---|---|---|---|---|
| Set-up time (hours) | Drying time (hours) | | | Set-up time (hours) | Drying time (hours) |
| 3.0 | 5.25 | Inositol | 6 | 3.3 | 8.25 |
| 2.75 | 8.0 | Inositol | 5 | 4.5 | 8.0 |
| 3.75 | 8.0 | Inositol | 4 | 8.5 | 13.0 |
| 3.33 | 5.8 | Pinitol | 5 | 3.5 | 6.25 |
| 5.75 | 8.25 | Pinitol | 4 | 15.0 | 15.5 |
| 11.5 | 17.0 | Pinitol | 3 | 12.0 | 14.0 |
| 3.0 | 7.5 | Quebrachitol | 5 | 4.0 | 6.5 |
| 3.3 | 9.0 | Quebrachitol | 4 | 6.6 | 9.0 |
| 10.0 | 18.5 | Quebrachitol | 3 | 5.6 | 9.0 |
| 3.3 | 6.0 | Mono-pentaerythritol | 4 | 2.6 | 2.6 |
| 4.25 | 5.5 | Di-pentaerythritol | 6 | 1.5 | 2.0 |
| 2.5 | 3.0 | Tri-pentaerythritol | 8 | 1.5 | 3.0 |
| ...... | 24.0+ | Glycerol | 3 | .... | .... |
| 3.25 | 4.33 | Erythritol | 4 | 1.75 | 2.25 |

THE set and dry times of the several families of cyclitol esters were in direct relationship to the number of fatty acids esterified per molecule. The cyclitol ester films showed somewhat better gloss and toughness than those of the pentaerythritol series although the differences between the tripentaerythritol esters and the cyclitol esters were marginal.

The drying and set times of the bodied oils are also shown in Table V. The Sanderson dry and set times of the bodied esters of $Z_2$ viscosity indicate quite conclusively that the pentaerythritol esters dry faster and obtain a harder set at an earlier time than do any of the bodied esters from the various cyclitols. The set and dry times of the bodied pentaerythritol esters are far superior to those of any of the other esters studied in this series.

It was pointed out previously concerning the heat polymerization of these oils that the hydroxyl content of the cyclitol esters decreases during heat processing. Dehydration of the cyclitol esters may occur in such a manner that an aromatic or cyclic olefin structure results. If the former is a diphenol type, it may act as drying inhibitor, and this may be a partial explanation for the delayed drying and set times shown by the heat-bodied cyclitol esters compared with the heat-bodied pentaerythritol esters.

In brief summary then, pinitol and quebrachitol esterify with linseed fatty acids at a rate somewhat slower than glycerol and faster than inositol. The esterification rates, physical, chemical, and film drying properties of the esters of these two cyclitols appear to be almost identical. The viscosities of the cyclitol esters are in all cases greater than those of the pentaerythritol esters when measured at the same degree of polymerization. The cyclitol esters have drying times similar to those of the corresponding monopentaerythritol esters and a little slower than those of the dipentaerythritol ester. Film toughness is similar to that of tripentaerythritol esters. Heat-bodying of pinitol and quebrachitol esters reduces their drying speed. This latter effect is in contrast to that observed with pentaerythritol esters, which dry more rapidly after heat polymerization.

### Acknowledgment

The authors gratefully acknowledge the assistance given by W. F. McKusick and Georgiann C. Krause in securing the data in this paper.

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[Received January 21, 1954]

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# Letter to the Editor

DEAR SIR:

Our attention has been drawn to the article by R. C. Stillman entitled "The Color Committee," which appeared in your March issue.

Mr. Stillman has inadvertently criticized the Lovibond system of color measurement when in fact his criticisms were really directed against the Wesson method, which has been used by the A.O.C.S. for many years.

Color is a subjective sensation which exists only in the mind of the observer, and when a customer agrees to pay a certain price for a certain colored oil, his only interest is "what does this color look like." He is not in the least interested in a series of figures which give the transmission at certain selected wavelengths because, firstly, these figures cannot possibly convey to the ordinary person what the color looks like and, secondly, two different colored liquids with entirely different transmission figures may look exactly the same to the average observer. Conversely, two sets of figures which appear very closely similar one to the other may represent very different visual colors. Hence the first point which we would make is that in this particular case of the valuation of an oil on its color, it is a statement of *what it looks like* that is required.

Color is, of course, three-dimensional, and the Lovibond system measures color in all three dimensions whereas the Wesson method for simplicity's sake ignores the brightness factor and seeks only to measure the degree of redness. The difficulties to which Mr. Stillman refers are caused by this over-simplification.

Mr. Stillman very truly remarks that the one thing that has not changed in 40 years is the Lovibond scale, and the oil industry in resisting a change has shown its wisdom in anchoring its standardization method to a scale of such rock-like stability.

As your previous Color Committee chairman reported last year, the difficulty of obtaining agreement between instruments employing spectrophotometric methods appears insuperable, and we submit that the use of a simple visual color standard for the practical men in industry has no rival.

Yours truly,

THE TINTOMETER LTD.
G. J. CHAMBERLIN
Managing Director
Salisbury, England

April 8, 1954

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DEAR SIR:

In reply to Mr. G. J. Chamberlin's letter of April 8, the Color Committee chairman has written Mr. Chamberlin to the effect that the Color Committee chairman has no criticism of the Lovibond system of color measurement *per se:*

> The Color Committee of the A.O.C.S. has been seeking for a long time to develop a color method which eliminates the personal equation. In order to do this, an instrumental method is required. In all instrumental methods, difficulties with instrument response are encountered. Serious consideration needs also to be given to these factors. They should be measured and taken into account in the resultant color equation. The work still goes on in the search for an ideal system of color measurement.
>
> One of the biggest criticisms of the use of Lovibond type in a Wesson colorimeter for measuring oil colors is the fact that apparent red values are reduced when chlorophyll is present in the oil. The second criticism is based on the fact that visual comparisons must be made. The Color Committee finds no fault with the Lovibond system of color measurement. The Color Committee only seeks to show why the use of the Wesson system with Lovibond glasses is inadequate for evaluating an oil and seeks to find a more satisfactory method for the evaluation.

R. C. STILLMAN, chairman
Color Committee

June 4, 1954