Synthesis of Conjugated Fatty Oils
III. Metallic Oxides as Isomerization Catalysts*

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THE desirable properties of fatty oils, such as Chinawood Oil, that contain conjugated systems of double bonds are well known. A previous paper (1b) described the use of siliceous materials as catalysts for the isomerization of double bonds in unsaturated fatty oils and acids so as to produce conjugation. The present report deals with the use of metallic oxides as catalysts for the same reaction.

Some metallic oxides have been reported in the hydrocarbon literature as isomerization agents for isolated dienes. Thus, "Activated Alumina"* has been shown to catalyze the transformation of 1,5-hexadiene to 2,4-hexadiene (2, 3), of 1,5-heptadiene to 2,4-heptadiene (2), and of various branched-chain isolated diolefins to their conjugated isomers (2). Chromium oxide has been used in the isomerization of 1,5-hexadiene (4), and a mixed catalyst of chromium oxide on aluminum oxide has been used in the treatment of a series of straight and branched-chain isolated diolefins (5). In the field of fatty oils, Scheiber (6) mentions, in a broad sense, the use of metallic oxides as isomerization catalysts, but supplies no experimental data. His American patent (6a) does not mention any specific oxide used; his British patent (6b), however, cites aluminum oxide and mercuric oxide.

Catalysts and Methods of Treatment

THE metallic oxides used in this work were "Activated Alumina," aluminum oxide, oxides of Group VI-A and oxides of Group IV of the Periodic System. Important differences in magnitude of catalytic effects were encountered among the several oxides used. In addition to such chemical differences, the physical properties of the catalytic material constitute a significant factor in determining the extent of the isomerization reaction. Catalytic activity is exhibited, in general, by amorphous forms of the metallic oxides; and such activity is further enhanced by greater available surface area in specially activated oxide catalysts. Similar observations were made in the case of siliceous catalysts (1b), and are, in fact, generally recognized in catalytic chemistry (7).

The isomerization reaction is best carried out by heating the unsaturated fatty oils or acids with the catalysts at about 250°C., with agitation, in an inert atmosphere, and under substantially anhydrous conditions. A ratio of about five grams of catalyst to 100 grams of oil or acids is advantageous for batch processes such as those reported here.

Experimental Results

Alumina Catalysis. One hundred grams of linseed oil fatty acids, which had previously been distilled and freed from saturated acids by chilling and filtering, were placed together with five grams of activated alumina in a glass reaction vessel. The catalyst was Aluminum Ore Company Grade A Activated Alumina, 8-14 mesh. The mixture in the reaction vessel was evacuated and flushed with nitrogen several times, so as to provide an inert atmosphere. This mixture was then heated at 250°C. for four hours, at atmospheric pressure, with agitation. At the end of this reaction period the mixture was cooled, the fatty acids were decanted from the catalyst, and the changes which had taken place were observed.

The experiment was repeated using a non-activated form of powdered aluminum oxide, in order to observe the effect caused by the activation of the catalyst. The results obtained are shown in Table 1.

TABLE 1
Isomerization of Linseed Acids by Alumina

Catalytic Treatment	Refractive Index n_D^{25}	Molecular Refraction, M.R.
None	1.4700	83.64
Non-activated alumina, 4 hours, 250°C	1.4728 (+0.0028)	84.06 (+0.42)
"Activated Alumina," 4 hours, 250°C	1.4781 (+0.0081)	84.88 (+1.24)

These property changes, which were not accompanied by any significant increase of viscosity, show that both forms of aluminum oxide bring about an increase in the amount of conjugated double bond constituents, but that the activated catalyst is considerably more effective than the non-activated form.

The refractive index data may be compared with similar data reported in the literature for shifting double bonds by other catalytic conditions. Bradley and Richardson (8) showed that three hours aqueous alkali isomerization of linseed acids produces a change in n_D^{25} from 1.4690 to 1.4803, or +0.0113. This was calculated to represent for the isomerized acids a total of 49.2% of conjugated constituents. The increase in refractive index in the "Activated Alumina" catalyzed reaction, therefore, shows a formation of about 35% of conjugated constituents.

The exaltation of molecular refraction may be compared with known exaltations for pure compounds of definite constitution. Thus, for a simple case, the isomerization of 1,5-hexadiene to 2,4-hexadiene produces an exaltation of molecular refraction of 1.7 (2). A conjugated heptadiene showed an exaltation of 1.9. Thus the exaltation exhibited as a result of the "Activated Alumina" treatment of linseed acids, 1.24, showed significant conjugation.

Oxides of Group VI-A. Under experimental conditions similar to those described for the alumina catalysis, the oxides, either alone or supported on a carrier, of the metals of Group VI-A of the Periodic System may be used. These catalysts include chro-

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*A registered trade-mark of the Aluminum Ore Company.

mium oxide, molybdenum oxide, and tungsten oxide. The catalyst carrier may be alumina.

One hundred grams of linseed oil fatty acids, which had previously been distilled and freed from saturated acids by chilling and filtering, were treated with five grams of ⅛" chrome- alumina activated catalyst tablets under conditions similar to those described above. The length of time of treatment, however, was varied so as to determine the effect of time of treatment on the relative degree of conjugation obtained. The results are shown in Fig. 1, and they indicate that a reaction time of 6 hours is the optimum duration of treatment under these experimental conditions. No significant change in viscosity or color was observed.

The same catalyst and technique are directly applicable to linseed oil itself, as well as to the fatty acids. However, the direct isomerization of the oil is more difficult, and, under the same catalytic conditions, the magnitude of the effect is less for the oil than it is for the fatty acids.

Oxides of Group IV. One hundred grams of linseed oil fatty acids, which had previously been distilled and freed from saturated acids by chilling and filtering, were treated with five grams of oxides of various metals of Group IV of the Periodic System. The experimental conditions were similar to those described for the alumina catalysis. The results obtained are shown in Table 2.

TABLE 2

Isomerization of Linseed Acids by Oxides of Metals of Group IV

Catalytic Treatment	Refractive Index n_D^{25}	Molecular Refraction, M.R.
None	1.4700	83.64
Germanium dioxide, 4 hours, 250°C	1.4719 (+0.0019)	83.96 (+0.32)
Zirconium dioxide, 4 hours, 250°C	1.4727 (+0.0027)	84.06 (+0.42)
Thorium dioxide, 5 hours, 250°C	1.4742 (+0.0042)	84.27 (+0.63)

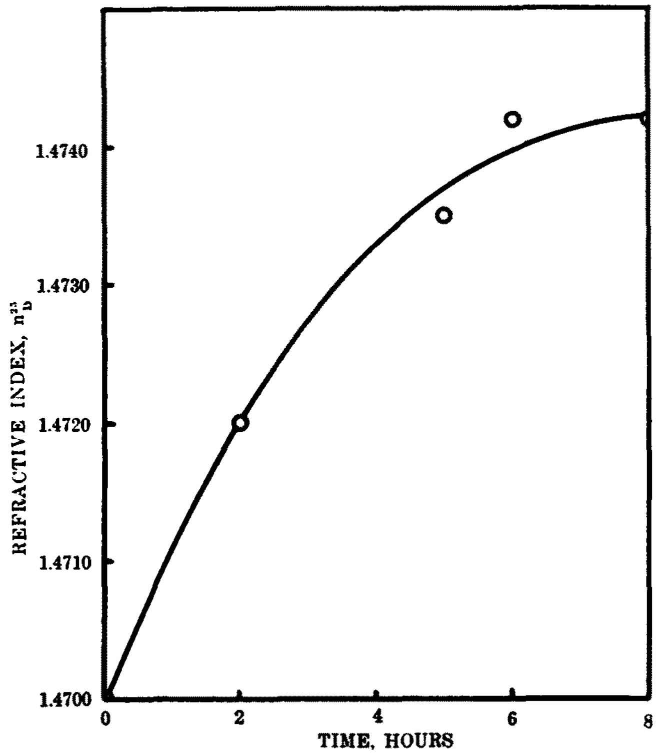

FIG. 1. Isomerization of Linseed Acids by Chrome-Alumina.

These property changes, unaccompanied by significant changes in viscosity or color, indicate increases in the percentage of conjugated constituents, and show that, for the substances and experimental conditions employed, the catalytic effect was greater for the oxides of higher molecular weight.

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Flavour Reversion in Linseed Shortening[1]

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Introduction

THIS study was undertaken in an effort to improve hydrogenated linseed oil for use as an edible fat to help meet the shortage in Canadian supplies. Preliminary work had indicated that although a shortening of apparently good quality could be produced, the products baked with this shortening, e.g., pastry or toasted bread, had a disagreeable flavour, commonly referred to as a reverted flavour.

The term "reverted" has been commonly used to describe a group of "off" odours which develop on heating or storing certain oils. Although it suggests the return of a flavour or odour which has previously been removed, this implication is incorrect and misleading, especially in the case of linseed shortening because the flavour and odour are different from any which were present either in the crude or the refined oil or in the freshly hydrogenated shortening. It should also be pointed out that, while reversion in an oil proceeds through a succession of different odours

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