STUDIES ON THE POLYMERIZATION OF LINSEED OIL

BY

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1- INTRODUCTION

Linseed oil is produced locally mainly for the production of the drying oil needed for paints, varnishes and other coating materials.

The properties of drying oils varied markedly depending on the variability of conditions of processing, driers and conditions of heating.

Unfortunately, the standard propencies of drying oil suggested by the Ministry of Industries are not sufficiently precise to lead to a complete control on the different products of drying oils.

The main test for drying oils is directly related to its drying properties.

Such a situation necessitates a thorough study of the different driers needed for the polymerization of linseed oil. Moreover a more detailed study on the polymerization of linseed oil with special reference to its U.V. spectroscopy may in fact throw light on the possibility of finding out the suitable method of producing superior types of polymerized linseed oil.

The present investigation deals mainly with the following three points :

1- The effect of heating and blowing air through linseed oil at 60, 90 and 120°C for 40 hours and the samples were subjected to the determination of physical and chemical properties.

2- The presence of driers in the concentrations 0.3 % and 0.6 % on the physical and chemical properties with special reference to polymerization. The driers include cobalt and manganese octanoate, cobalt sulfate, manganese oxide, a mixture of cobalt octanoate and manganese octanoate and a mixture of cobalt sulfate and manganese oxide.

3- Ultraviolet examination of various samples as a means of identification of conjugated systems and the degree of polymerization under the various conditions conducted during the course of the present investigation.

II- REVIEW OF LITERATURE

Linseed oil is the most widely used drying oil in the U.S.A. The successful use of linseed oil in the field of painting is due to its ability and efficiency to form dry, tough, and durable dry films when exposed to air in thin layers.

Linseed oil represents the back-bone of various products of drying oils used in manufacturing paints, varnishes and linoleum.

The literature dealing with linseed oil is quite enormous to be completely covered in this thesis and only the points related to this work is thoroughly reviewed.

Linseed oil was investigated from the standpoint of the best conditions of polymerization which include heating treatments and catalysts to produce blown oil with excellent qualities at the lowest possible expenses.

A- EFFECT OF HEATING AND BLOWING AIR ON THE PHYSICAL AND CHEMICAL PROPERTIES OF LINSEED OIL.

Remington (1946), noted that blowing air through linseed oil increased its specific gravity, acidity and viscosity. Oxygen in blown air adds at first to the double bonds of the unsaturated siguts forming unstable compounds followed by secondary oxidation with the subsequent formation of aldehydes and acids.

Mattiello (1947), reported that during the transformation of the liquid oil into a solid film, there are three primary reactions taking place; oxidation of the unsaturated compounds, polymerization of oxidized molecules and gelation or coagulation of this polymerized colloidal system.

It is needless to mention that the rate of oxidation of linseed oil is very slow at first, due to the induction period caused by natural antioxidants.

O'Hare (1949), found that after an induction period of about two hours, the logarithm of viscosity of the oil increased linearly with the reaction time during thermal polymerization of linseed oil.

In practice, the time required for blowing drying oils is quite dependent upon the length of the induction period which precedes rapid oxidation and to a lesser extent upon the rate of the reaction.

Blom (1949), noted that heating linseed oil at 180 - 190°C for about 10 hours increased the molecular weight and decreased the iodine value.

Bailey (1951), indicated a simple operation for the production of blown oil from crude linseed oil where a vigorous current of air was blown through the heated oil until the product with the desired viscosity was formed. Blowing linseed oil at elevated temperatures leads to further polymerization of the oil and the operation is usually carried out up to a certain point depending on the particular uses of the product.

Grummitt (1955), referred to the current theory of thermal polymerization of oil containing nonconjugated double bonds (i.e. Linseed oil and soybean oil), which involve isomerization on heating so that a fraction of the ethylenic groups become conjugated. Polymerization then proceeds via the Diels-Alder additive reaction between the 1, 3 - diene group in one acid radical and the double bond in the other.

Sims (1955), considered the Diels-Alder reaction, a suitable explanation for the formation of the gigantic molecular size of polymerized linseed oil.

Sutton (1955), noted that the thermal treatment of linseed oil, and unsaturated type of oils, could turn the oil to polymerized and polycondensate products, formed through the formation of covalent linkages between fatty acid chains i.e. a polymer of the original triglycerides, and such products are utilized in the synthesis of surface coating materials.

Triebs (1956), studied oxygen absorption by unsaturated sights of the oils and stated no hydroperoxide and ethylenic groups are produced which could offer a logical explanation to the increase in the ester number which takes place during the drying process.

Gunstone (1958), reported that linseed oil when heated at about 300 C, suffered marked increase in viscosity which took place slowly at first and then more rapidly, until a very thick liquid was formed.

in this reaction an increase in density, refractive index and mean molecular weight is observed when the characteristic properties of the products are formed, while their iodine values decreased rapidly at first and then at a slower rate. It was further known (Gunstone 1958), that during polymerization there was a development of conjugated unsaturation and conversion of Cis - to Trans-olefinic groups.

Pascual (1966), studied the properties of oils due to polymerisation by the use of radioactive tracer techniques to detect and follow some of the changes occuring during the thermal treatment of drying oils. He found a decrease in the number of carbon-carbon double bonds which was interpreted in terms of a reaction, probably polymerization, which sets in after the induction period. The polymerisation is probably a Diels-Alder type involving polyunsaturated compounds. The possibility exists that intramolecular polymerization is involved in the initial phase of the reaction which is followed by internal polymerisation.

Hirs (1967), studied through I.R. spectroscopy the influence of experimental conditions during alkyd resin temperature on the cis-trans isomerization of the unsaturated acids. An increase in temperature from 240 to 260°C caused isomerization of linseed oil, but the effect on soybean oil is much less marked.

Boelhauwer (19[illegible]7), noted that the glyceride and polyglycerides present in thermally polymerized linseed oils could be determined quantitatively by molecular distillation. The analysis of fatty acid indicates the appearance of intra-and inter molecular condensation. Internal conditions lead to the formation of bicyclic dimeric fatty acid groups with the original glycerides without an increase in the molecular weight and such an effect was less marked with soybean oil.

Kuska (1968), heated linseed oil at 270°C for 12 hours in the presence of carbon dioxide without any catalyst or solvent. Then the linseed fatty acid methyl ester was prepared by the usual method. Cyclic monomers were obtained from the vacuum distillate (187/ 0.2 - 1.2 mm) of the ester by the urea adduct separation. Most of the cyclic monomers belong to the cyclohexane type of derivatives.

Giovanni (1966), stated that the thermal polymerization of linseed oil at 200°C under gaseous nitrogen yielded mixtures of dimers and trimers, which were separated by partition chromatography on silicic acid or cellulose and characterized by their characteristic gas chromatograms.

5- EFFECT OF DRIERS ON THE PHYSICAL AND CHEMICAL PROPERTIES OF LINSEED OIL :

Long and Ball (1936), used hydrogen chloride as a catalyst in polymerization of fatty acids.

Farben (1939), noted that the metallic soaps proved to be quite effective in the thermopolymerization of linseed oil, since they improved the drying properties of the oil. Lead, nickel, cobalt, iron and manganese soaps are looded upon as successful promotors of this type of reaction. The common radical is the linoleate, oleate, naphthenate and resinate groups.

Furrans (1946), found that the reaction during blowing of the heated oil is influenced by various factors including temperature, free fatty acids, light