NEW METHODS OF PREPARATION OF EPOXIDIZED OILS AND THEIR INDUSTRIAL APPLICATIONS

Thesis Submitted to
Faculty of Science
Ain Shams University

By

BADRAN MOHAMED AHMED BADRAN
B.Sc. (Hons.), M.Sc.

For

The Degree of Ph.D.
(Chemistry)

National Research Centre
Dokki - Cairo
Arab Republic of Egypt

1 9 7 3

NEW METHODS OF PREPARATION OF EPOXIDIZED OILS

AND THEIR INDUSTRIAL APPLICATIONS

Thesis Advisers

Prof. Dr. G. E. M. Moussa

Prof. Dr. N. A. Ghanem

Approved

. . . .

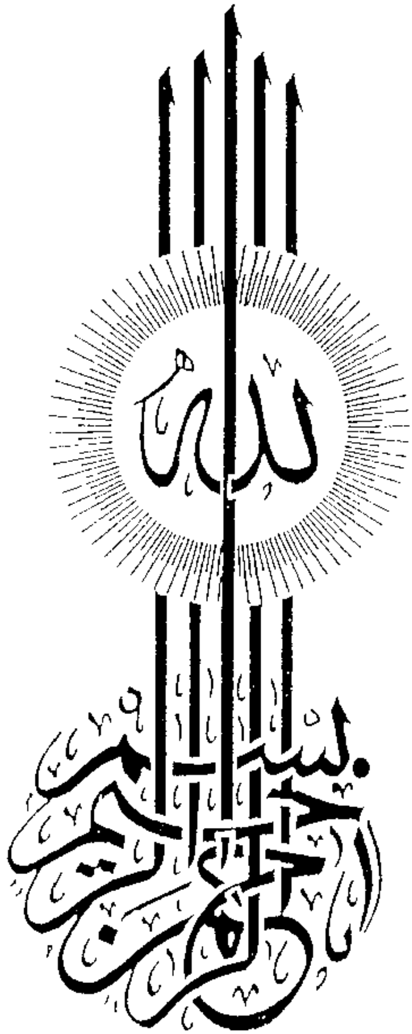
N. A. Ghanem

Prof. Dr. S. K. Tobia

Head of Chemistry Department,

Faculty of Science,

Ain Shams University.


بسم الله الرحمن الرحيم

A C K N O W L E D G M E N T

This record of research work was carried out in the Laboratory of Polymers and Pigments of the National Research Centre in Cairo. The problems involved were suggested by Dr. N. A. Ghanem, Professor of Polymer Technology at the National Research Centre. The author wishes to express his many thanks, and sincere appreciation for his valuable guidance and helpful criticism throughout the course of the work.

The author is also glad to thank Prof. Dr. G. E. M. Moussa, of the Chemistry Department, Faculty of Science, Ain Shams University, for his valuable help and interest of this work,

Thanks are also due to Dr. A. B. Moustafa and Dr. E. M. Abdel-[illegible] of this Laboratory for their valuable assistance and helpful suggestions during the work.

My thanks are [illegible] extended to the research colleagues and assistants at the Laboratory of Polymers and Pigments and other laboratories for their co-operation in various ways.

CONTENTS

Page

THE AIM OF WORK

Among the main interests of this Laboratory is the development of synthesis, processes and product application in the various fields of macromolecules. Among the synthesis already published in the field of surface coatings are the preparation of certain oil-modified alkyd resins **for use** as water-thinnable vehicles for paints. Examples of new processes are to be found in our work on the glycerolysis, dehydration, water-solubilization of oils as well as on ester interchange in monomers and the acetylation of acetylene to produce vinyl acetate. In most of the above processes ion exchange resins were introduced as insoluble catalysts and co-catalysts and very useful results were obtained.

The aim of the present thesis is to extend the above work by using ion exchange resins in other processes and finding new applications of the product. It is decided from the beginning to proceed in such a way that the technological and the economical aspects would go hand in hand. For example, ion exchange resins of natural origin are to be employed in place of costly synthetic ion exchange resins, and the non-edible castor oil is to be used instead of edible oils. After dehydration, the fatty chain of castor oil will contain two double bonds which provide suitable sites for further reactions.

The work concentrates on the catalytic process of epoxidation of dehydrated castor oil which, as it appears from the literature, has not been well studied. It is also intended to find new applications for the epoxidized oil after suitable treatments and mixing with additives. It is hoped to extend the known uses of epoxidized oils as plasticizers and stabilizers to surface coatings of unique qualities employing the fact that the epoxy group is polymerizable. It is also hoped to make epoxidized oils double acting by reacting the reactive epoxy groups with suitable reagents; a product containing large fatty chains and an aromatic secondary amine might be useful as plasticizer-antioxidant in rubber formulations.

Summary of Results

In this thesis advancements in three related fields were achieved:

1- The epoxidation of dehydrated castor oil (D.C.O.) was studied, using as catalyst both natural (lignin sulphonic acid; modified Lignosite) and synthetic (crosslinked poly-styrene sulphonic acid; Zeo-Karb 225) ion exchange resins. Beginning with epoxidation of oleic acid, which contains one double bond per fatty chain to represent a simple component of the triglycerides, it was found that modified Lignosite failed as an epoxidation catalyst for oleic acid while Zeo-Karb 225 was effective. Epoxidation was then extended to D.C.O. It was found that Zeo-Karb 225 was a more efficient catalyst than modified Lignosite.

2- The possibility of using epoxidized D.C.O. in the surface coatings field was studied in detail. The trials depended upon polymerizing epoxidized D.C.O. through the epoxide rings by the action of $SnCl_4.5H_2O$. Thus involving the use of small proportions of a melamine resin minimized the tackiness of the films. The studies showed that the films made of epoxidized maleinized D.C.O. had almost no tackiness at all. It was found that stoving the epoxidized maleinized oil with 0.75% catalyst ($SnCl_4.5H_2O$) on wt. of oil at 170°C for 1 - 1½ hours gave films of excellent appearance and favourable physical and mechanical properties. In addition the films had excellent resistance to alkali solutions.

3- The reaction of epoxidized D.C.O. with two diamines - ethylenediamine and p-phenylenediamine - was studied in detail. It was found that increasing the amount of amine over 5% was practically of no effect. Preliminary investigations aiming at introducing the reaction product of epoxy oil and p-phenylenediamine as a combined plasticizer-antioxidant agent in rubber formulations, was found to be of some value meriting further studies.

SECTION A

INTRODUCTORY CHAPTERS

CHAPTER I

EPOXIDATION AND EPOXIDES

CHAPTER I

Introduction:-

Epoxidation is the introduction of the three-membered epoxide ring into an unsaturated organic compound. The resulting products are usually quite reactive and there are a large number of potential and actual uses for them. The peracid ($R.CO_3H$) is the responsible reagent for the epoxidation process. There are two general methods for the epoxidation of unsaturated compounds. The first one is the separate (old) epoxidation technique, in which the peracid is prepared in separate, followed by reacting the peracid with the compound to be epoxidized. The second one is the in-situ technique, where the peracid is prepared during the epoxidation process, The rate-determining step is the step of the formation of peracid[1].

The earlier work indicated that the peracetic acid could not be used for epoxilation, but it has become the most widely used peracid since 1945 because conditions for obtaining high yields of epoxides with a minimum of side reactions were developed[2-4] and it has been commercially available since 1947 as a 40% solution in acetic acid[5]. Other advantages are that, it has a high epoxidation efficiency and a reasonable level of stability at ordinary temperatures. Epoxidation of unsaturated compounds with peracetic acid can be conducted in aqueous, nonaqueous, homogeneous and heterogeneous media[6]. Several hundred unsaturated compounds can be epoxidized with peracetic acid.

Facile and high-speed preparation of peracetic acid or performic acid by the reaction of hydrogen peroxide with acetic or formic acid respectively, has led to the development of in-situ epoxidation methods. In these, almost complete utilization of hydrogen peroxide is achieved[6], while the separate method results in a waste as much as 20% of available active oxygen[7], thus, the in-situ technique is the most economical.

In the preparation of peracid, either in separate (old) or in-situ technique, solid cation exchange resins are most desirable because they promote the peracid, do not promote by-product formation and minimize epoxide ring opening. Cation exchange resins of low metal content specially heavy metals are the best[7-9]. An advantage for cationic exchange resins over sulphuric acid is that they can be easily separated from the reaction medium by filtration or decantation; the

The reaction is of wide applications with respect to both the peroxy acid and the olefin and is often refferred to as the Prileshajew reaction[14,15].

The rate of epoxidation varies inversely as the water content of the peracid increases. The increase of the concentration of hydrogen peroxide used improved the oxirane content of the product[16,17]. The lowest hydroxyl content was achieved by using anhydrous peracetic acid in ethyl acetate[16], or by use of dry peracetic acid in acetic acid[18].

Products with theoretical oxirane content could not be obtained even for oleic acid derivatives due to the predomenance of side reactions[19], but under suitable reaction conditions high quality epoxidized oils could be prepared even by dilute hydrogen peroxide[19]. Thus, the epoxidized product contains mainly epoxy compound, but contains small quantities of unsaturated doulbe bonds and acetoxy hydroxy compounds[2].

Effect of Solvents on the Epoxidation Process:- Solvents also affect the rate of epoxidation, but the mechanism of their action is not clear[20-23]. Attempts to correlate solvent