THESIS

ENTITLED

SYNTHESIS AND EVALUATION OF SOME NEW POLYMERIC PLASTICIZERS

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CONTENTS

Page

Page

Page

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AIM OF THE WORK

The objective of this work is to prepare high molecular weight plasticizers and polymeric plasticizers for polyvinyl chloride (PVC) from naphthenic acids, or naphthenic alcohol with glycol, dibasic acids.

The naphthenic acids or alcohols are synthesized from a pertoelum fraction rich in naphthenes, b.r. 170-250°C, from Balaim Crude Oil.

The properties imparted to polyvinyl blends by these plasticizers are compated with the commercial imported plasticizer to examine feasibility of their preparation, utilization and replacement of the imported plasticizers.

SUMMARY

It is recognized that each group of polymers has its own plasticizers to improve their properties although some types of plasticizers have been developed which are suitable for several plastics. These plasticizers belong to the groups of esters, ketones, ethers, epoxides and nitrogen containing compounds like sulphonamides.

Not one known plasticizer can fulfil all the properties demanded for practical applications.

Liquid plasticizers with good plasticization properties are likely to show bad aging properties due to volatility, migration on storage for long periods.

This is only one reason why the plastics industry is working towards polymeric and high molecular weight plasticizers with expected greater permanance, no volatility, migration, extraction ... etc.

The purpose of the present work is to prepare high molecular weight and polymeric compounds using the Egyptian petroleum fraction with a boiling range of 170-250°C as a source for the synthesis of some new polymeric plasticizers.

This fraction was dewaxed with urea and then dearomatized with oleum.

This fraction was oxidized in the liquid phase at different air flow rates, with various catalysts (cobalt and manganese resinates) in presence and absence of nitrogen oxides as initiators to naphthenic acid. Maximum yield of acids was obtained with these oxides. A part of the naphthenic acid was esterfied to methyl ester which were then reduced to the corresponding naphthenyl alcohol.

Di-B-hydroxyl alkyl esters of dibasic acids were prepared. Naphthenic acid was then reacted with these esters to give the corresponding di-B-naphthene carboxyalkyl esters of the type:

$$R''COO - R - OOC - R'' - COOR - OOC\ R''$$

Where,

R = Alkylene bridge of ethylene glycol, 1,2 propylene glycol.

R' = Alkylene bridge of the dibasic acid, succinic, glutaric or adipic acid.

R" = Naphthene moiety in naphthenic acid.

The naphthenic acid was also treated with diols and dibasic acids to give a series of polymeric compounds of the type polyalkylene glycol polyalkylene dicarboxylate, terminated naphthenic acid of the type:

$$N - G - (A - G)_n - N$$

Where,

A = Dibasic acid, succinic, glutaric or adipic acid.

G = Ethylene glycol or 1,2 propylene glycol.

N = Naphthenic moiety in naphthenic acid.

n = Number of repeating units in the molecule and equals to 5.

Another series of the polymeric compounds of the type poly alkylene dicarboxylate polyalkylene glycol terminated naphthenyl alcohols;

$$L - A - (G - A)_n - L$$

Where,

L = Nephthenyl moiety in naphthenyl alcohol, and n has the same above value.

were also prepared by treating naphthenyl alcohol with the same dibasic acids and diols. It was found that the theoretical molecular weights of the prepared compounds agreed fairly well with those obtained by saponification equivalent as well as by ebullioscopic method.

All the prepared compounds were tested as plasticizers for polyvinyl chloride.

The main conclusions deduced from this work may be summerized as follows:

1- Mechanical properties:

- The high molecular weight and polymeric compounds exhibit higher values of tensile strength and 100% tensile strength than di-n-octyl phthalate (DNOP) excpect in the case of the polymeric polyadipate polyethlene glycol termonated naphthenyl.

- Higher values of tensile strength and 100% tensile stress were obtained with the increase of the number of carbon atoms in the plasticizers molecules.

- These compounds elongate the vinyl chloride blends to about the same degree of elasticity.

- Hardness measurements indicate that these compounds soften the vinyl blends.

The most notable difference between these compounds and (DNOP) were in volatility and resistance to kerosine extraction.

2- Volatility loss:

All the prepared compounds have less weight loss than the blends when plasticized with (DNOP).

3- Kerosine extraction:

Blends containing (DNOP) were much more extracted by kerosine while those blended with the high molecular weight compounds or polymerics showed little weight loss.

4- Loop compatibility test:

High molecular weight and polymeric compounds vinyl blends showed no sign of exudation on subjection to the loop compatibility test. In this respect, they were good compatibe materials to PVC.

Generally, all the high molecular weight compounds and polymerics exhibited improved permanence properties over the commercial plasticizer (DNOP).