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Saad A. Fam^a

^a Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

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Some High Molecular Weight Phthalate Plasticizers for Poly (Vinyl Chloride) Resins

SAAD A. FAM

Egyptian Petroleum Research Institute
Nasr City, Cairo, Egypt

ABSTRACT

Naphthenic acids and alcohols were prepared by oxidation of naphthenes. Four different high molecular weight phthalates of the types bis-2-naphthene carboxyethyl phthalate and ethylene glycol bis(naphthenyl phthalate). These high molecular weight phthalates and di-n-octyl phthalate (DNOP), as a reference commercial plasticizer, were compounded with poly(vinyl chloride) (PVC) and evaluated as plasticizers. The high molecular weight phthalates were more sensitive to soapy water than DNOP. Volatility and resistance to kerosene extraction studies were markedly better than for DNOP. The new plasticizers have good compatibility with PVC resin.

INTRODUCTION

High molecular weight plasticizers can be made from dicarboxylic acids, glycols, and monocarboxylic acids or monohydroxy alcohols. They have rapidly found their way into uses where migration and extraction resistance are important [1]. In many cases these plasticizers are used as secondary plasticizers in the plastics industry.

The aim of this work is to prepare high molecular weight phthalate plasticizers for poly(vinyl chloride) (PVC) from phthalic anhydride, glycol, or ethylene chlorohydrin and naphthenic acids or naphthenic alcohols. These naphthenic acids or alcohols are synthesized from a petroleum fraction rich in naphthenes. The properties imparted to vinyl blends by these plasticizers are compared with those of blends plasticized with the commercial plasticizer DNOP.

EXPERIMENTAL

Preparation of Naphthenic Acids

n-Paraffins and aromatics-free "Balayim" crude oil fraction boiling at 160-240°C were oxidized in the liquid phase with air at a flow rate of 5 L/(min-100 g hydrocarbon) in the presence of KMnO_4 (0.2 g/100 g hydrocarbon) as catalyst at 130, 140, 150, and 160°C [2]. The naphthenic acids so obtained were fractionated under vacuum into two fractions (A and B, Table 1).

Preparation of Naphthenic Alcohols

The methyl esters of naphthenic acids A or B were reduced with hydrogen under an initial pressure of 100-200 atm using copper chromite (CuCr_2O_4) catalyst at 150-250°C to the corresponding alcohols (C and D, Table 2).

Preparation of Potassium Naphthenate

Naphthenic acid (0.3 mol) and powdered KOH (0.3 mol) were heated at 90-100°C with stirring for 1 h. Drying at this temperature in vacuum afforded a reddish brown paste of potassium naphthenate.

Preparation of Acid Ethylene Glycol Diphthalate

A mixture of phthalic anhydride (0.6 mol) and ethylene glycol (0.3 mol) was heated at 160-180°C for 30 min. On cooling, the solid product was crystallized from acetone to give the acid ethylene glycol diphthalate, mp 157-158°C [3].

TABLE 1. Characteristics of the Naphthenic Acid Fractions A and B

Acid fraction	bp, °C/ 4 torr	D_4^{20}	η_D^{20}	Acid no.	Av MW ^a [6]
A	96-135	0.9256	1.4330	311	181
B	136-171	0.9462	1.4618	258	216

^aEbullioscopic in benzene.

TABLE 2. Characteristics of Naphthenic Alcohol Fractions C and D

Alcohol	bp, °C/ 4 torr	D_4^{20}	η_D^{20}	OH no.	Av MW
C	72-109	0.8614	1.4288	334	168
D	108-151	0.8863	1.4549	276	203

Preparation of Bis(2-chloroethyl) Phthalate

A mixture of phthalic anhydride (0.5 mol), ethylenechlorohydrin (1.5 mol), and concentrated H_2SO_4 (98%, 10 mL) was refluxed for 6 h. After cooling, the reaction mixture was poured onto ice water (300 g), extracted with ether (400 mL), and dried over anhydrous magnesium sulfate. The ether was distilled off under vacuum to give bis(2-chloroethyl) phthalate [4].

Preparation of Bis-2-naphthenecarboxyethyl Phthalate

Potassium naphthenate of either the acid A or B (0.3 mol) and bis(2-chloroethyl) phthalate (0.15 mol) was heated under dehydrating conditions at 140-150°C for 12 h. The reaction mixture was cooled, dry benzene (300 mL) was added, it was allowed to stand for 30 min, and the precipitated potassium chloride was filtered off. The solvent was then distilled off, and the resulting oily ester was purified by distillation under reduced pressure and then characterized (Table 3).

TABLE 3. Physical Properties of High Molecular Weight Phthalate Plasticizers

Plasticizer	Yield, %	bp, °C/2 torr	D_4^{20}	η_D^{20}	Av MW	
					Theoretical	Ebullioscopic
LBNP ^a	64	123-171	1.0322	1.4718	580	556
HBNP ^b	62	173-212	1.0455	1.4832	650	634
LENP ^c	70	118-159	1.0128	1.4703	658	642
HENP ^d	65	156-206	1.0326	1.4821	728	710

^aLBNP = bis-2-naphthenecarboxyethyl phthalate obtained from low boiling range naphthenic acids.

^bHBNP = bis-2-naphthenecarboxyethyl phthalate obtained from high boiling range naphthenic acids.

^cLENP = ethylene glycol bis (naphthenyl phthalate) obtained from low boiling range naphthenyl alcohols.

^dHENP = ethylene glycol bis (naphthenyl phthalate) obtained from high boiling range naphthenyl alcohols.

Preparation of Ethylene Glycol Bis(Naphthenyl Phthalate)

Naphthenyl alcohol (C or D, 0.6 mol), acid ethylene glycol diphthalate (0.3 mol), 10 mL concentrated sulfuric acid (98%), and dry benzene (300 mL) were refluxed for 8 h. After cooling, the reaction mixture was poured on ice-cold water and stirred well for 10 min. After drying, the benzene solvent was distilled off under reduced pressure. The resulting ester was purified by simple distillation under vacuum. Its characteristics are given in Table 3.

Performance of Various High Molecular Weight Phthalates and DNOP in Plasticization of PVC

The following PVC formulation was used throughout this work: PVC, Enichem Product, low molecular weight; epoxidized linseed oil of oxirane (oxygen content, 5.5%), prepared in situ by epoxidation [5], 5 part/100 parts of resin (phr); stearic acid, 0.5 phr; basic lead carbonate, 1.0 phr; and plasticizer, 40 phr.

The composition was fluxed on a differential speed roll mill for 8 min at 150°C, then molded into test plaques at 160°C for 5 min at 10.4 MPa. Thereafter, tests for mechanical properties, volatility, soapy extraction, kerosene extraction, and compatibility were applied.

RESULTS AND DISCUSSION

Optimum yield of naphthenic acids (16-19 wt% of the starting fraction) can be attained by liquid-phase air oxidation of naphthenes-rich fractions at 140°C using KMnO_4 as catalyst. The synthesized naphthenic acids are fractionated into low and high boiling fractions (L and H, Table 1). Each fraction is subjected to conversion into the potassium salt and reduction of the methyl esters with hydrogen.

The maximum yield of alcohols (89-93%) was obtained at 200 atm hydrogen pressure and 200°C (Table 2). The infrared spectrum of the alcohols shows absorption peaks at 3 530-3 500 cm^{-1} for OH groups. The potassium salt reacts with bis(2-chloroethyl)phthalate to give high molecular weight phthalates of the type bis-2-naphthene-carboxyethyl phthalate (LBNP and HBNP, Table 3). The acid ethylene glycol diphthalate reacts with the naphthenyl alcohol to produce the corresponding ethylene glycol bis(naphthenyl phthalate) (LENP and HENP, Table 3).

The resulting high molecular weight phthalates are oily liquids, generally of a pale yellow or amber color with an agreeable smell. Their molecular weights were calculated theoretically and determined

TABLE 4. Performance of Various Plasticizers and DHOP

Plasticizer properties ^a	LBNP	HBNP	LENP	HENP	DNOP
Ultimate tensile strength, MPa	23.6	20.0	24.1	21.0	20.8
100% modulus, MPa	15.2	13.8	15.8	14.7	14.3
Elongation at break, 100%	230	250	210	240	250
Hardness, Shore A	83	80	78	82	74
Activated carbon volatility, % loss at 70°C for 24 h	0.3	0.2	0.3	0.2	1.5
Soap water extraction, 1% Ivory soap, 20 h, 70°C, wt%	4.8	3.9	4.6	3.5	3.3
Kerosene extraction, 24 h, 23°C, wt%	1.3	0.7	1.8	1.1	46.9
Compatibility, 3/8" loop test exudation, 24 h	None	None	None	None	None

^aTensile data by ASTM D638. Shore hardness A by ASTM D 676. Loop compatibility by ASTM D 3291.

ebullioscopically (Table 3). In general, it was found that molecular weights determined ebullioscopically agree fairly well with the theoretical molecular weights. IR spectra of the prepared phthalates shows strong bands at $1\ 780\text{--}1\ 720\ \text{cm}^{-1}$ for $-\text{COO}$ groups.

Data for resin blends plasticized with the prepared phthalates are listed in Table 4. HBNP imparts slightly lower values of tensile strength and 100% modulus than the other high molecular weight phthalates and DNOP. DNOP offers a slight improvement in hardness and ultimate elongation over the prepared phthalates. Table 4 also indicate that the new plasticizers are more sensitive to soapy water than DNOP. The most notable differences are in volatility and resistance to kerosene extraction, where the prepared phthalates demonstrate a marked advantage, especially HBNP. The data in Table 4 also show that all the high molecular weight phthalates are good compatible plasticizers for PVC.

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