

Isocyanate-Modified Dehydrated Castor Oil

R.N. MUKHERJEA, K.K. SAHA, A. GUPTA, and S.K. SANYAL, Chemical Engineering Department, Jadavpur University, Calcutta - 700032, India

ABSTRACT

Esters of dehydrated castor oil fatty acids with polyhydric alcohols like ethylene glycol, propylene glycol, glycerol, pentaerythritol and sorbitol have been prepared. The esters, having hydroxyl value ranging from 78.5 to 167, were reacted with toluene diisocyanate. The scratch hardness and other film properties of the resulting urethanes have been studied. Urethanes obtained from various mixtures of the above esters also have been studied. The best results have been obtained when a mixture of ethylene glycol ester and pentaerythritol ester of dehydrated castor oil fatty acids in the ratio of 4:1 are reacted with one equivalent of toluene diisocyanate. One equivalent of glycerol ester (hydroxyl value 78.5), ethylene glycol ester (hydroxyl value 167), or propylene glycol ester (hydroxyl value 159.4) of DCO fatty acids when reacted with 1.25 equivalent of toluene diisocyanate also gave satisfactory products.

INTRODUCTION

Isocyanate-modified oils are among the first urethane materials to find any practical industrial application. The reaction of isocyanates with hydroxy products derived from drying oils was made use of by Bayer (1) to obtain film-forming materials, which are superior in many respects to oil-modified alkyd resins. In 1951, Robinson and Waters (2) obtained urethane oils by reaction of polyols of linseed oil or dehydrated castor oil (DCO) with hexamethylene diisocyanate. Products of good stability, drying rate and satisfactory physical and mechanical properties were obtained, although they exhibited poor color characteristics, inferior flow and durability.

Castor oil and modified castor oils were employed by Pansing (3), Patton (4,5) and Malyan (6) for satisfactory urethane oil coatings. Preparation and evaluation of such urethane oils have been reported by many other workers (7-15). Balakrishna et al. (16) reported that the use of 1.25 moles of toluene diisocyanate per two moles of DCO diglyceride (hydroxyl value 89.3) resulted in gelling, while one mole of toluene diisocyanate per 2 moles of diglyceride gave satisfactory products. Misra et al. (17) reported that

the hydroxyl value of alcoholized vegetable oils was the controlling factor in film performance.

Although extensive work has been done on urethane oil-based coatings, a systematic study of modified, dehydrated castor oil-based urethane oils appears not to have been done yet. In the present investigation, esters of varying hydroxyl values, derived from DCO, have been used for urethane oil formation, with a view to determining the most suitable hydroxyl value of a DCO ester for their applications. In this context, the prepared esters of DCO fatty acids and ethylene glycol, propylene glycol, glycerol, pentaerythritol, and sorbitol have been studied.

MATERIALS AND METHODS

Chemically pure grade ethylene glycol (Pfizer), 1:2, propylene glycol (British Drug House), pentaerythritol (B.D.H.), sorbitol (Pfizer), dibutylamine (E. Merck), glycerol and toluene diisocyanate (TDI), 80:20 (Bayer).

Castor oil: refractive index 1.476 (25 C), density (d_{28}^{28}) 0.9555, viscosity (20 C) 9.86 poise, acid value 1.2, hydroxyl value 168, iodine value 88.2, saponification value 190.4.

DCO obtained by dehydration of castor oil at 210-220 C with 1.5% sodium bisulfate as dehydrating agent and 0.5% of sodium bisulfite as antipolymerizing agent (18): refractive index 1.4818 (25 C), density (d_{33}^{33}) 0.9346, color R = 1, y = 5, viscosity (20 C) 3.08 poise, acid value 4, hydroxyl value 26.6, iodine value 136, diene value 15.7, saponification value 200.

DCO fatty acids prepared by refluxing 200 g DCO with 200 ml 25% ethanolic potassium hydroxide followed by acidification and extraction with ether: refractive index 1.4658 (25 C), density (d_{30}^{30}) 0.9076, color R = 0, y = 10.2, viscosity (20 C) 1.23 poise, neutralization value 184, hydroxyl value 54.3, diene value 21.3, iodine value 143.

Esters of DCO Acids (16,19) were prepared in a 500 ml three-necked flask, fitted with a stirrer, thermometer and arrangement for bubbling N₂, using 150-200 g dehydrated castor oil fatty acids. Reaction time, corresponding temperature and catalyst used are listed in Table I. The product was allowed to cool to room temperature and diluted with ether; for sorbitol and pentaerythritol esters it was filtered. Ethylene glycol ester, propylene glycol ester, and glycerol esters were then neutralized with aqueous sulfuric acid and

TABLE I

Reaction Conditions for Different Esters Derived from DCO

Sample No.	Product	Reactants	Mole ratio acid (or DCO):polyol	Temperature °C	Time in hr	Catalyst %
1	Glycerol esters	A. DCO + Glycerol B. -Do- C. -Do-	1:0.52 1:0.69 1:0.8 1:2.7	230-240	3	0.1 KOH -Do-
2	Ethylene glycol ester of DCO acids	DCO acids + Ethylene glycol		170-185	6	-Do-
3	Propylene glycol ester of DCO acids	DCO acids + Propylene glycol	1:1.76	175-185	6	-Do-
4	Pentaerythritol ester of DCO acids	DCO acids + Pentaerythritol	3:1	220-240	3	No catalyst
5	Sorbitol ester of DCO acids	DCO acids + Sorbitol	4.5:1	195-200	6	0.25 (Ca acetate: Ba acetate = 3:1)

TABLE II
Physicochemical Properties of Different Esters Derived from DCO

Sample No.	Product	Color	Viscosity 20 C, cps.	Refractive index (25 C)	Density (g/cc)	Acid value	Hydroxyl value	Iodine value	Equivalent weight (based on OH value + acid value) (g)
1	Glycerol ester-A	R = 3 Y = 10.1	666	1.4823	d_{28}^{28} 0.9466	1.1	78.5	106.2	704.77
2	Glycerol ester-B	R = 3 Y = 8.1	1163	1.4825	d_{29}^{29} 0.9588	1.2	102.6	107.7	540.98
3	Glycerol ester-C	R = 3 Y = 7.2	1400	1.4829	d_{30}^{30} 0.9629	2	121.4	107.8	454.61
4	Ethylene glycol ester	R = 3.6 Y = 4	106.6	1.4742	d_{30}^{30} 0.9408	7.6	167	110	321.3
5	Propylene glycol ester	R = 3.1 Y = 6	149.3	1.4802	d_{31}^{31} 0.9303	7.9	159.4	100	335.32
6	Pentaerythritol ester	R = 3.6 Y = 10.1	2280	1.4847	d_{30}^{30} 0.9634	0.5	124.2	102.6	449.88
7	Sorbitol ester	R = 4 Y = 5.6	1862	1.4845	d_{25}^{25} 0.9656	18.8	78.5	114	576.6

TABLE III
Reaction Conditions for Different Urethane Oils and Their Physical and Chemical Properties

Sample No.	Component	Ratio of ester/ TDI	Reaction time hr	Viscosity 20 C, poise (1:1 white spirit soln)	Color	Acid value	OH value	% of NCO	Surface dry hr	Drying time Hard dry hr	Tack free dry hr
1	Glycerol ester-A	1:1.25 eq.	4	6.03	R = 2.6 Y = 8.1	0.8	20	0.81	0.25	1	3
2	Glycerol ester-B	1:1 eq.	4	10.95	R = 2.8 Y = 10	1.6	42.5	0.35	0.50	4	24
3	Glycerol ester-C	1:1 eq.	3	Spongy mass							
4	Ethylene glycol ester	1:1 eq.	4	5	R = 3 Y = 4.1	1.7	27.2	0.38	0.50	4	Tacky
5	Ethylene glycol ester	1:1.25 eq.	3	Solution is pasty	R = 2.4 Y = 5	1	8.2	1.1	1	4.15	24
6	Propylene glycol ester	1:1 eq.	4	5.95	R = 2.8 Y = 5.8	2	33.6	0.50	0.30	3.30	Tacky
7	Propylene glycol ester	1:1.25 eq.	3	Solution is pasty	R = 2.4 Y = 5.5	1	9.8	1.41	0.40	4	24
8	Pentaerythritol ester	1:0.7 eq.	0.30	Spongy mass							
9	Sorbitol ester	1:1 eq.	1	Spongy mass							

TABLE IV
 Physical and Chemical Properties of Mixed Urethane Oils^a

Sample No.	Weight ratio of components	Color	Viscosity 20C, poise (1:1 white spirit soln)	Acid value	Hydroxyl value	% of NCO	Surface dry hr	Drying time Hard dry hr	Tack free dry hr
10	Glycerol ester-A + Pentaerythritol ester (4:1)		Spongy mass						
11	Ethylene glycol ester + Pentaerythritol ester (4:1)	R = 2.8 Y = 4	16.6	0.7	19.6	0.27	0.30	3	30
12	Propylene glycol ester + Pentaerythritol ester (4:1)	R = 2 Y = 5.1	43.9	2	18	0.23	0.25	3.40	30
13	Ethylene glycol ester + Sorbitol ester (4:1)	R = 3.4 Y = 10	Solution is pasty	1.4	29	0.44	1	3	Tacky
14	Propylene glycol ester + Sorbitol ester (4:1)	R = 3.1 Y = 4.6	-Do-	2.4	21	0.32	1	5	Tacky
15	Glycerol ester-B + Pentaerythritol ester + Ethylene glycol ester (1:1:8)	R = 2.6 Y = 12	-Do-	0.9	33.4	0.45	1	6	40

^aReaction time 4 hr (using 1:1 eq. = Ester/TDI).

washed with water till free from glycols and acid. For glycerol esters DCO was used. In all cases, ether was distilled off and the last traces removed by mild heating under vacuum.

Physicochemical properties of the esters derived from DCO are listed in Table II.

Analytical Methods

Color: Lovibond tintometer, 10 mm cell; viscosity: Oswald viscometer; refractive index: AOCS method (Cc 7-25); density: by specific gravity bottle; acid value: AOCS method (F 9a-44); hydroxyl value: AOCS method (Cd 4-40); saponification value: AOCS method (Cd 3-25); diene value: Ellis and Jones method (AOCS method Ka 12-55); iodine value: Wijs method (30 min, AOCS method Cd 1-25); NCO determination: modified method of Siggia and Hanna (20).

Preparation of Urethane Derivatives

For preparation of urethane derivatives, the DCO ester sample (25g) was taken in a three-necked flask fitted with a sealed stirrer, a thermometer, and a dropping funnel, through which the required amount of toluene diisocyanate was added in drops during half an hour. The temperature was maintained at 90-95 C with good stirring for the lengths of time listed in Tables III and IV. The product was cooled and kept for 24 hr to ensure the stabilization of the product.

Film Characteristics

The drying and film characteristics of the samples were determined after addition of cobalt and lead naphthenates (Co 0.05%, Pb 0.5% based on metal). White spirit was added to bring down the viscosity of the urethane oil to between 1 and 3 poise. Scratch hardness, solvent, and chemical resistance properties of the films were observed after 48 hr (Tables III to V). Scratch hardness was determined by Dupond Scratch Testing Machine on films of 20-25 μ thickness and the effect of solvent and chemicals was observed by immersion of glass panels in the appropriate reagent at room temperature.

RESULTS AND DISCUSSION

Earlier workers had pointed out that the diglyceride of

DCO is suitable for the preparation of urethane oil. Since it is not possible, in practice, to prepare a glyceride which contains only diglyceride molecules, it may be important to determine the average hydroxyl value of a glyceride that is suitable for the preparation of a good urethane oil. A glyceride having hydroxyl value up to 102.5 is found in our experiment to be suitable for the preparation of urethane oil, using toluene diisocyanate (1:1 eq), while a glyceride having a hydroxyl value of 121.4 gelled within 3 hr during the progress of the reaction.

Since urethane oils prepared from hydroxyl esters of high functionality showed increased tendency for gellation, lower molecular weight products were prepared. In the case of ethylene glycol ester and propylene glycol ester, gellation has not been observed, although these require larger amounts of toluene diisocyanate (1:1 eq.) due to their higher hydroxyl values as compared to glycerinated DCO. However, the films obtained from these urethane oils are tacky. It was also observed that by using 1.25 eq. toluene diisocyanate per equivalent of ethylene glycol ester or propylene glycol ester, comparatively satisfactory urethane oil can be obtained. On the other hand, pentaerythritol ester and sorbitol ester caused gellation within 0.5 to 1 hr and finally gave a spongy mass.

Urethane oils from ethylene glycol ester and propylene glycol ester, when mixed with pentaerythritol ester in the ratio of 4:1, gave excellent films, having good solvent and chemical resistance properties. Blending with sorbitol ester in the same proportion does not, however, give good film properties, probably because of the hygroscopic nature of sorbitol. A blend of glyceride B, pentaerythritol ester and ethylene glycol ester(1:1:8) reacted with 1 eq. toluene diisocyanate also gives urethane oil of good film characteristics, although with slower drying properties. In the case of a mixture of glyceride A and pentaerythritol ester (4:1), gellation is observed.

All the samples gave glossy films except for the sorbitol ester/ethylene glycol ester or propylene glycol ester blend. The color of the urethane oil samples was superior to that of the original esters, and the films obtained were slightly yellow and transparent.

Urethane oil from ethylene glycol ester and pentaerythritol ester blend (4:1) shows no change in viscosity even

TABLE V
Properties of the Urethane Coatings

Sample ^a No.	Scratch hardness	Effect of solvent and chemicals ^b						5% Sodium carbonate
		Water	White spirit	Xylene	Butanol	2% Sulphuric acid		
1	900 g	N.E. (24 hr)	N.E. (24 hr)	F.D. (1 min)	S.B. (30 min)	N.E. (24 hr)	N.E. (10 hr)	
2	800 g	S.B. (1.15 hr)	N.E. (24 hr)	F.D. (1 min)	F.D. (16 min)	N.E. (24 hr)	S.B. (6 hr)	
5	1000 g	N.E. (24 hr)	N.E. (24 hr)	S.B. (1.20 hr)	B (16 min)	N.E. (24 hr)	N.E. (24 hr)	
7	1000 g	N.E. (24 hr)	N.E. (24 hr)	S.B. (30 min)	B (15 min)	N.E. (24 hr)	N.E. (24 hr)	
11	1000 g	N.E. (24 hr)	N.E. (24 hr)	B (5 min)	S.B. (40 min)	N.E. (24 hr)	S.B. (3.30 hr)	
12	800 g	N.E. (24 hr)	N.E. (24 hr)	F.D. (3 min)	N.E. (1 hr)	N.E. (24 hr)	S.B. (1 hr)	
13 ^c	400 g	N.E. (24 hr)	N.E. (24 hr)	B (8 min)	N.E. (1 hr)	N.E. (24 hr)	B (3.30 hr)	
14 ^c	500 g	N.E. (24 hr)	N.E. (24 hr)	B (5 min)	B (30 min)	B (3.30 hr)	B (24 hr)	
15	1000 g	N.E. (24 hr)	N.E. (24 hr)	B (4 min)	N.E. (1 hr)	N.E. (24 hr)	N.E. (24 hr)	

^aSame as in table III and IV.

^bN.E. = no effect; F.D. = films detached; S.B. = slight blushing; B = Blusing.

^cFilm obtained after 10 days. The figures given in the brackets indicate the time after which the particular effect takes place.

after one year, while the storage stability of other compositions is also quite satisfactory.

ACKNOWLEDGMENT

Toluene diisocyanate was donated by U-foam Ltd., Hyderabad, India. One of the authors (KKS) obtained a UGC Fellowship.

REFERENCES

1. Bayer, O., *Angew Chem.* 59:257 (1947); BIOS Report No. 628, Item 22, 18.
2. Robinson, E.B., and R.E. Waters, *J. Oil Colour Chem. Assoc.* 34:361 (1951).
3. Pansing H. E., *Off. Dig., Fed. Paint Varn. Prod. Clubs* 30(396):37 (1958).
4. Metz, H.M., A. Ehlich, M.K. Smith, and T.C. Patton, *Paint Oil Chem. Rev.* 121:6 (1958).
5. Patton, T.C., and H.M. Metz., *Off. Dig.* 32:222 (1960).
6. Malyan, C.R., *Paint Technol.* 24(272):17 (1960).
7. Symposium on Polyurethane Coatings, *Ind. Eng. Chem.*, 51:1381 (1959).
8. Shearing, H.F., *Paint Oil Color J.* 143:191 (1963).
9. Stanton, J.M., *JAOCS* 36:503 (1959).
10. Goldblatt, L.A., *Ibid.* 39:502 (1962); and C.K. Lyon, *Ibid.* 40:157 (1963).
11. Welsted, H.L., *Paint Varn. Prod.* 52(11):50 (1962).
12. Toone, G.C., *Paint Technol.* 27(1):38 (1962).
13. Griffith, J.A., and G.E. Rohl., *Off. Dig.* 36:117 (1964).
14. Toone, G.C., *Austr. Paint J.* 8(7):11 (1962).
15. Jolly, A.C., *J. Oil and Col. Chem. Assoc.* 47:919 (1964).
16. Balakrishna, R.S., H. Dakshinamurthy, and J.S. Aggarwal, *Paint India*, 15(9):24 (1965).
17. Misra, J.P., M.A. Sivasamban, *Paint Manuf.* 41(12):30 (1971).
18. Achaya, K.T., *JAOCS* 48:758 (1971).
19. "Bailey's Industrial Oil and Fat Products," 3rd Edition, Edited by D. Swern, Interscience Publishers, New York, 1964, p. 518.
20. Shulman, S., W.M. Formo., and A.E. Rheineck, *JAOCS* 38:205 (1961).

[Received September 25, 1978]