Emulsifiers Derived from Linseed Oil and Their Potential Use in Coatings [1]

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Abstract

In the development of a stable linseed oil emulsion paint, a series of emulsifiers were prepared from linseed oil and its fatty acids and alcohols: (a) linseed monoglycerides, (b) mono- and dilinseed fatty sorbitan esters and a mixed ester obtained by the transesterification of linseed oil with sorbitol, (c) polyoxyethylene ether adducts formed by reacting ethylene oxide with these sorbitan esters, and (d) linseed polyoxyethylene ether made by ethoxylation of linseed alcohols. Another series of surfactants was prepared by esterifying a polyoxyethylene ether of sorbitol with various amounts of linseed fatty acids. Conditions of preparation and pertinent physical and chemical properties of the emulsifiers are given.

Some of these emulsifiers demonstrated film-forming properties. Combinations were formulated into linseed oil emulsion paints with and without zinc oxide. Paints containing zinc oxide have been relatively stable in viscosity for about 2 yr.

Introduction

THE NORTHERN LABORATORY in cooperation with the National Flaxseed Processors Association has undertaken a program of research on linseed oil emulsion paints. It was agreed that reactive emulsifiers should be developed because they could polymerize and become part of the film. Accordingly, reactive emulsifiers were prepared and evaluated in linseed oil emulsion paints.

Benefits that might accrue if higher concentrations of emulsifiers could be used without increasing the water sensitivity of the coating are suggested frequently in the current literature. H. L. Jaffe and J. H. Fickenscher (6) state that too finely divided clay leads to coagulation during a freeze-thaw cycle because the increased surface of the clay is slightly starved for surface active material. F. J. Hahn (4) suggests that the agglomeration of pigment and latex particles caused by the action of thickeners can be prevented by an increase in the concentration of surface active agents. Hilliard and Srail (5) conclude that the higher pigment volume concentration possible in solution paints, as compared to emulsion paints, results from the smaller particle size of the vehicle in the solution paint. Increased concentration of surface active agent should lead to smaller particle size of the vehicle, should give better dispersion of the pigment and should make it possible to have a higher pigment volume concentration in emulsion paints. Some of our results obtained with reactive emulsifiers in linseed oil emulsion paints have been reported previously (8).

Preparation of Linseed Emulsifiers

Linseed monoglycerides were prepared by the method of Mattil and Sims (9). The crude product contained 73% α-monoglyceride. Two molecular distillations increased the α-monoglyceride to 93%.

A mixed linseed monoglyceride monolinseed sorbitan ester was made by alcoholysis of 1 mole of linseed oil with 2 moles of sorbitol.

The method of Griffin (3) was followed in making the mono- and dilinseed sorbitan esters and their polyoxyethylene derivatives.

Oleyl polyoxyethylene ether and linseed polyoxyethylene ether were made from oleyl and linseed alcohol, respectively, by adding ethylene oxide according to Karabinos et al. (7).

Polyoxyethylene sorbitol and its linseed esters were prepared by reacting sorbitol with ethylene oxide and subsequent esterification. Fine (1) suggests that this procedure yields sorbitol derivatives rather than its anhydrides.

Table I lists the details of the preparation of 12 emulsifiers. Two of these, oleyl polyoxyethylene ether and polyoxyethylene sorbitol, were not reactive toward oxygen in our tests. The former was included for comparison and the latter was used as an inter-

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TABLE I
Preparation of Linseed Emulsifiers

Emulsifier	Charge in moles			Cooking schedule		Catalyst	
	Fatty acids	Polyol	Ethylene oxide	Temp, C	Time, hr	Material	G
Alcoholysis							
Linseed monoglyceride	0.57[a]	5.40	......	120	1	$NaOCH_3$	5.0
Mixed linseed monoglyceride and monosorbitan esters	0.16[a]	0.32	......	230–40	5	$NaOCH_3$[b]	1.1
Polyoxyethylation							
Oleyl polyoxyethylene ether	......	0.25[c]	3.70	170–80	9	KOH[b]	0.4
Linseed polyoxyethylene ether	......	0.50[c]	8.10	190	10	KOH[b]	0.7
Polyoxyethylene monolinseed sorbitan ester	......	0.10	1.57	130–45	13	$NaOCH_3$[b]	0.9
Polyoxyethylene dilinseed sorbitan ester	......	0.09	2.00	140–55	10	$NaOCH_3$[b]	0.14
Polyoxyethylene sorbitol	......	1.00	19.50	140	15	KOH	1.0
Esterification							
Monolinseed sorbitan ester	0.40	0.44	......	230–40	4	NaOH[b]	0.2
Dilinseed sorbitan ester	0.30	0.15	......	230–40	2	NaOH[b]	0.1
Polyoxyethylene sorbitol monolinseed ester	0.20	0.20	......	170	90	KOH[d, e]	......
Polyoxyethylene sorbitol dilinseed ester	0.40	0.20	......	170	10	KOH[d, e]	......
Polyoxyethylene sorbitol trilinseed ester	1.50	0.50	......	170	50	KOH[d, e]	......

[a] Linseed oil.
[b] Catalyst was removed by neutralization with HCl in nonaqueous media and filtration through Celite bed.
[c] Alcohol.
[d] Treated with carbon (Darco G-60).
[e] Residual catalyst from ether preparation.

mediate for the linseed esters. The chemical characteristics of the emulsifiers are shown in Table II.

Table III reports specific gravity, viscosities, and aqueous surface tension. Viscosities were determined with a Cannon-Fenske-Ostwald viscometer and surface tensions with a du Noüy tensiometer. These surface tensions show the products are in the emulsifier range with the exception of polyoxyethylene sorbitol.

Solubilities of the emulsifiers in a variety of solvents were studied at 1% concentration by weight (Table IV).

TABLE II

Chemical Characteristics of Linseed Emulsifiers

Emulsifier	Acid no.	Sap. no.	I.V. (Wijs)	Ethylene oxide, moles/mole
Linseed monoglyceride	0.4	151.0	151.0	......
Mixed linseed monoglyceride and monosorbitan esters	0.6	140.0	136.0	......
Oleyl polyoxyethylene ether	......	......	23.8	15
Linseed polyoxyethylene ether	......	......	41.5	16
Polyoxyethylene monolinseed sorbitan ester	0.7	51.0	40.0	16
Polyoxyethylene dilinseed sorbitan ester	0.5	72.4	54.6	21
Polyoxyethylene sorbitol	......	......	......	20
Monolinseed sorbitan ester	2.0	127.0	128.9	......
Dilinseed sorbitan ester	0.2	157.0	155.0	......
Polyoxyethylene sorbitol monolinseed ester	4.1	46.5	36.8	20
Polyoxyethylene sorbitol dilinseed ester	3.0	74.8	69.7	20
Polyoxyethylene sorbitol trilinseed ester	1.7	94.9	89.4	20

Film-Forming Properties of Linseed Emulsifiers

To test film-forming properties of these emulsifiers, a basic emulsion was compounded by mixing the following ingredients in the order listed:

Emulsifier	7 g
Pb-Co driers	4 drops
5% Ammonium dipicolinate in ethylene glycol	4 drops
Water	3 g
Xylene	4 g

The drier solution was made of 71.5% lead naphthenate, containing 24% lead, and of 28.5% cobalt naphthenate, containing 6% cobalt. Four drops of this solution resulted in approximately 0.6% lead and 0.06% cobalt based on the emulsifier. These emulsions were drawn on 3¼ in. × 4¼ in. glass slides with a doctor blade to a wet film thickness of 0.005 in. The "water test" described by Schwab et al. (10) was used after the films had dried 1 month (Table V).

Films containing polyoxyethylene washed off in the water test except those prepared with polyoxyethylene sorbitol trilinseed ester. The best film was formed from the dilinseed sorbitan ester. It also oxidized the

TABLE III

Physical Properties of Linseed Emulsifiers

Emulsifier	Specific gravity at 25C	Viscosity at 25C[a]	Surface tension,[b] dynes/cm Conc., wt % in water			
			1.0	0.1	0.01	0.001
		cp				
Linseed monoglyceride	......	solid	......	......	31	34
Mixed linseed monoglyceride and monosorbitan esters	1.010	1,000	......	31	37	56
Oleyl polyoxyethylene ether	......	solid	42	43	44	48
Linseed polyoxyethylene ether	......	solid	39	39	40	43
Polyoxyethylene monolinseed sorbitan ester	1.090	676	39	41	44	54
Polyoxyethylene dilinseed sorbitan ester	1.059	391	42	42	46	57
Polyoxyethylene sorbitol	1.204	1,077	64	67	69	70
Monolinseed sorbitan ester	1.004	1,470	......	32	37	63
Dilinseed sorbitan ester	0.984	307	......	......	49	67
Polyoxyethylene sorbitol monolinseed ester	1.113	895	40	42	45	53
Polyoxyethylene sorbitol dilinseed ester	1.069	551	39	44	47	57
Polyoxyethylene sorbitol trilinseed ester	1.032	275	......	48	55	69

[a] Cannon-Fenske-Ostwald viscometer.
[b] du Noüy tensiometer.

TABLE IV

Solubilities of Linseed Emulsifiers at 1% Concentrations

Emulsifier	Water		Solvents					
	0.1%	1.0%	Benzene	Ethyl ether	Acetone	Methyl alcohol	Mineral spirits	Linseed oil
Linseed monoglyceride	I	I	S	S	S	S	S	S
Mixed linseed monoglyceride and monosorbitan esters	D	I	S	S	S	S	S	S
Oleyl polyoxyethylene ether	S	S	S	S	S	S	I	I
Linseed polyoxyethylene ether	S	S	S	S	S	S	I	I
Polyoxyethylene monolinseed sorbitan ester	S	S	S	I	S	S	I	S
Polyoxyethylene dilinseed sorbitan ester	S	S	S	S	S	S	I	S
Polyoxyethylene sorbitol	S	S	S	S	S	S	I	I
Monolinseed sorbitan ester	D	I	S	S	S	S	S	S
Dilinseed sorbitan ester	I	I	S	S	S	I	S	S
Polyoxyethylene sorbitol monolinseed ester	S	S	S	I	S	S	I	I
Polyoxyethylene sorbitol dilinseed ester	S	S	S	S	S	S	I	I
Polyoxyethylene sorbitol trilinseed ester	D	D	S	S	S	S	S	S

I—Complete insolubility. D—Dispersibility or cloudy emulsion. S—Clear solutions.

TABLE V

Tests on Linseed Emulsifier Films

Emulsifier	Description of film	Max wt gain, %	Water test (10)
Linseed monoglyceride	Soft, tacky	6.2	Opaque
Mixed linseed monoglyceride and monosorbitan esters	Soft, tacky	4.8	Very opaque
Oleyl polyoxyethylene ether	Greasy, no adhesion or cohesion	0.0	Washed off
Linseed polyoxyethylene ether	Soft,oily	1.0	Washed off
Polyoxyethylene monolinseed sorbitan ester	Soft, tacky, poor cohesion	3.3	Washed off
Polyoxyethylene dilinseed sorbitan ester	Soft, tacky, poor cohesion	4.9	Washed off
Polyoxyethylene sorbitol	Soft, greasy, poor cohesion	0.0	Washed off
Monolinseed sorbitan ester	Tacky, fairly cohesive	6.6	Slightly opaque
Dilinseed sorbitan ester	Hard, dry	9.9	Excellent resistance
Polyoxyethylene sorbitol monolinseed ester	Soft, tacky, poor cohesion	1.7	Washed off
Polyoxyethylene sorbitol dilinseed ester	Soft, tacky, poor cohesion	3.4	Washed off
Polyoxyethylene sorbitol trilinseed ester	Tacky, good cohesion and adhesion	4.6	Slightly opaque

most as indicated by the weight gain. This weight gain was oxidation and not moisture absorption since the films from oleyl polyoxyethylene ether and polyoxyethylene sorbitol did not show any weight gain under the test conditions.

Paints Made with Linseed Emulsifiers

One paint was made according to the following formula in which only emulsifiers were used for the vehicle:

Material	Weight, %
Water	28.38
Linseed polyoxyethylene ether	2.51
Ethylene glycol	0.27
Ammonium dipicolinate	0.01
Antifoam	0.13
Hydroxyethyl cellulose	0.02
Dilinseed sorbitan ester	18.82
Cobalt naphthenate (6% Co)	0.40
Mineral spirits	2.80
Rutile TiO_2 "Ti-Pure 610"	37.60
A.S.P. 400 clay	4.53
Mica mineralite	4.53

The paint contained 68% nonvolatiles and remained stable after storing for 25 months at 25C. It was compounded by adding all the water-soluble materials in the order listed to one-third of the water. The dilinseed sorbitan ester, cobalt naphthenate, and the mineral spirits were combined and then added to the water solution. The pigments were dispersed in the remaining two-thirds of the water, and the emulsion was added to the slurry. The emulsion was not stable until the pigment slurry was added. Although the sample was too small to determine viscosity, it had a dry-to-touch time of less than 30 min and a through-dry of 10 hr as determined on the Sanderson drier. It passed the water test after drying 1 hr. The paint had good brushing qualities and was easy to clean from the brush with water.

The following general formula was used to test several combinations of emulsifiers:

Material	Weight, %
Water	29.4
A.S.P. 400 clay	3.9
Mica mineralite	3.9
Rutile TiO_2 "Ti-Pure 610"	32.2
Hydrophilic emulsifier (Type I)	3.0
Hydroxyethyl cellulose W.P. 4400	0.3
Advance antifoam	0.05
Ethylene glycol	0.43
Ammonium dipicolinate	0.02
M-37 linseed oill	21.7
Ethyl cellosolve	2.4
Hydrophobic emulsifier (Type II)	2.4
Cobalt naphthenate (6% Co)	0.3

The paints were compounded by making slurries of the first nine ingredients and adding mixtures of the last four ingredients to these slurries.

The pairs of emulsifiers, types I and II, and their hydrophile-lipophile balance numbers (HLB) are shown in Table VI, calculated according to Griffin (2). The HLB range was from 9.1–13.2.

TABLE VI
Emulsifiers and Resulting Hydrophile-Lipophile Balance (HLB)

Paint no.	Hydrophilic emulsifier Type I	Hydrophobic emulsifier Type II	HLB
1	Commercial polyoxyethylene sorbitan monostearate	Commercial sorbitan monostearate	10.3
2	Polyoxyethylene dilinseed sorbitan ester	Dilinseed sorbitan ester	10.1
3	Commercial polyoxyethylene sorbitan mono-oleate	Commercial sorbitan mono-oleate	10.4
4	Linseed polyoxyethylene ether	Polyoxyethylene sorbitol trilinseed ester	13.2
5	Oleyl polyoxyethylene ether	Commercial sorbitan mono-oleate	9.7
6	Commercial oleyl polyoxyethylene ether	Commercial sorbitan mono-oleate	10.4

Table VII illustrates the paint viscosities and how they changed with time. The biggest percentage change in viscosity occurred in paint No. 4 (HLB of 13.2). A thirteenfold viscosity increase was observed.

TABLE VII
Viscosity *vs.* Age in Weeks of TiO_2 Linseed Emulsion Paints with Different Emulsifier Pairs

Paint no.	HLB	0 cp	6 cp	15 cp	36 cp	48 cp	107 cp
1	10.3	15,000	19,000	15,000	21,000	19,000	25,000
2	10.1	7,000	6,700	5,700	5,800	5,500	6,900
3	10.4	2,200	1,200	1,200	1,700	2,000	4,000
4	13.2	1,300	1,100	1,700	3,300	5,400	16,700
5	9.7	950	880	870	960	1,350	2,200
6	10.4	260	160	200	200	300	530

When driers and pigments were added to a stable linseed oil emulsion having an HLB of 14.2, a gummy paint exhibiting syneresis resulted. The most stable paints were with pairs of types I and II in the HLB range of 10–12.

Initial viscosities of the paints depended on the choice of emulsifiers as well as the HLB. The saturated stearate emulsifiers gave a paint of 15,000 cp at an HLB of 10.3, whereas the unsaturated oleates resulted in 2,200 cp at an HLB of 10.4. We are investigating the possibilities of controlling the paint viscosities by means of the choice of emulsifiers, thus eliminating the need for thickeners.

The increased stability of linseed oil emulsion paints containing zinc oxide and formulated with some of the linseed emulsifiers has been reported in detail (8).

First attempts to formulate M-37 linseed oil emulsion paints with ordinary commercial emulsifiers and a pigment in which zinc oxide was substituted for 37.5% of the weight of titanium dioxide resulted in emulsions that broke in about 30 min. Two paints based on the general formula but containing zinc oxide showed the viscosity *versus* time effects that are illustrated in Table VIII. Both paints had linseed polyoxyethylene ether as the type I emulsifier. Paint No. 1 had linseed monoglyceride as the type II emulsifier and had an HLB of 10.5; paint No. 2 had monolinseed sorbitan ester and had an HLB of 11.4.

TABLE VIII
Viscosity *vs.* Age of Linseed Emulsion Paints Containing Zinc Oxide and Different Emulsifier Pairs

Age, weeks	Brookfield viscosity at 20 rpm, cp	
	Paint no. 1	Paint no. 2
0	2,200	1,800
7	3,000	1,000
20	2,800	590
34	2,500	800
46	3,400	900
63	6,400	1,200
72	5,700	1,500
103	7,900	10,000
116	13,000	11,000
129	14,000	20,000

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