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ECOFRIENDLY LIQUID DETERGENTS BASED ON MALENISED VEGETABLES OILS

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ABSTRACT

Malenized Linseed oil suitable for use in liquid detergent has been synthesized. The reaction conditions such as mole ratio, temperature, time of reaction and use of catalyst have been standardized to get a product with desired HLB ratio, viscosity and solubility. A standard liquid detergent mainly based on malenised vegetables oils and Alpha olefin sulphonate has been prepared. In successive compositions acid slurry and sodium lauryl sulphate has been replaced by neutralized malenized linseed oil by 50 to 100%. A comparison of our maleic based detergents with commercial samples shows that maleic treated oils give excellent foaming, surface tension reduction and detergency properties. The raw material cost of our novel liquid detergents is reasonable and they can be tried on pilot scale and commercial scale production. The special feature of these liquid detergents is its freedom from conventional linear alkyl benzene sulphonate and sodium tripolyphosphate so they can be labeled as ecofriendly products for green environment.

Key words: Ecofriendly, Liquid detergent, Malenised vegetable oil.

INTRODUCTION

Malenised vegetable oils have been used in various industrial products like wall finishes[1], water thinnable paints[2], electro deposition paints[3], water thinnable primers[4] and printing inks[5]. We have already used malenized oil for production of liquid detergent[6] as well as lotions. Polymeric surfactants are an exciting new addition to the existing product range of surfactants. Polymeric surfactants when incorporated into detergent they offer following performance features.

(i) Ca and Mg sequesterization

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(ii) Clay soil disperancy

(iii) Calcium carbonate inhibition

(iv) Prevention of soil redeposit ion

(v) Fabric anti incrustation

In the present work, experimental conditions have been worked out for getting a novel polymer based mainly on linseed oil, coconut oil and maleic anhydride. The experimental conditions have been set up to get desired molecular weight, HLB ratio and detergency characteristics. Novel catalysts sodium bisulphate, sodium bisulphate and hydrochloric acid have been used in preparation of malenised oil.

The possible chemical reactions are addition reaction of maleic anhydride. When we heat the oil, a part of linolinic acid is converted to 9, 11, 13-octadecatrionoic acid by isomerisation; this conjugated acid reacts with maleic anhydride by Diels Alder reaction. The other reaction is direct addition of maleic anhydride at active methylene group.

EXPERIMENTAL

The reactor

The preparation of malenised oil was carried out in a glass reactor. The reactor consists of two parts. Lower part of the reactor is round bottom vessel with very wide mouth. The upper part of the reactor is its lid having four necks with standard joints. A motor driven stirrer was inserted in the reactor through the central neck, while another neck was used for thermometer a condenser was fitted with the reactor through the third neck. The fourth neck was used for dropping the chemicals into the reactor. An electric heating mantle having special arrangement for smooth control of the temperature (-/+2) has been used. A regulator controlled the speed of the stirrer.

Preparation of malenised oil

Initially linseed oil, coconut oil, maleic anhydride and catalyst were taken in glass reactor. The mass was heated slowly and steadily to 200^{o}C for about half an hour. This temperature was maintained for one hour. The reaction temperature was then raised to 230^{0}C and reaction was continued steadily for two hours at this temperature. Now steadily reaction temperature was lowered down to 150^{o}C and the reaction was continued at this temperature for two hours. The acid value and viscosity was observed periodically and reaction is terminated when desired acid value and viscosity was attained. Batch was withdrawn carefully & weighted to get % yield.

Neutralization of malenised vegetable oil

100 g of novel copolymer was heated to 70^{o}C and the calculated amount of KOH was added to this polymer with constant stirring so as to get slightly alkaline solution of polymer with pH 8.

Table 1: Composition of novel malenized oil (% by weight)

Ingredient	Batch No. 1 (M1)	Batch No. 2 (M2)
Linseed oil	45	86
Maleic anhydride	10	10
Coconut oil	40	--
Benzoic ocid	01	02
Oxalic ocid	02	02
Citric ocid	02	--
Catalyst used: 1.5% sodium Bisulphate, 0.5% sodium bisulphite and 1% Hydrochloric acid on weight of total mass.		

Heating schedule of malenization of oil

Procedure: Coconut oil or Linseed oil + Maleic anhydride + Sodium bisulphate + Sodium bisulphate + HCl

↓

Mixed all ingredients add to the reactor

↓

Heat up to 200^{0}C

↓

Maintain temperature for 1hour

↓

Heat at 230^{0}C for 2Hrs

↓

Maintain temperature for another at 2 hours 150^{0}C

↓

Cool at 60^{0}C

↓

Thin down the resin if required with Isopropyl Alcohol.

Total time of Heating : 5 Hrs and 30 minutes

Table 2: Physico-chemical properties of malenized oil

Test	M1	M2
% solid	97.46	97.65
Acid value	36.06	38.67
Viscosity (By ford cup No. 4 in sec.)	240	285
Color	Brown	Brown
Consistency	Thin	Thin
Solubility	Alcohol NaOH Xylene : butanol	Alcohol NaOH Xylene : butanol
pH value	2.71	2.7
Molecular weight	3360	3026
H.L.B. ratio	13.8	16.0
Saponification value	196.27	114.02
Epoxy value	1.6	1.8

Table 3: % Detergency of original polymer

Conc.	M1	M2	Acid slurry	Alpha olefin sulponate
0.1	82.0	81.0	62.00	58.20
0.25	87.0	84.0	66.50	63.60
0.5	93.0	89.0	70.85	69.80
1.0	97.0	95.0	85.00	83.33

Table 4: Variation in % detergency with pH

Batches	pH Values			
	Original	pH-8	pH-10	pH-11
M1	97	91	84	79
M2	95	91	78	66

Table 5: Liquid detergent based on these polymers

Ingredient	LD1	LD2	LD3	LD4	LD5
Sorbitol	10	10	10	10	10
Glyerine	10	10	10	10	10
Urea	03	03	03	03	03
Alpha olefin sulphonate	02	02	02	02	02
Neutralized polymer (100% solids)	--	M1 4.5	M1 9.0	M2 4.5	M2 9.0
Isopropanol	01	01	01	01	01
Water	54	54.5	55	54.5	55
Acid slurry	10	05	-	10	10
Sodium lauryl sulphate	10	10	10	05	--

Table 6: Physicochemical properties of liquid & commerical liquid detergent

Conc.	Sample	Foam volume in cm^3 (time in min.)				Density (gm/cc)	Surface tension (dyne/cm)
		0	5	10	15		
0.1%	LD1	600	550	500	400	0.875	40.12
	LD2	500	450	400	400	0.790	41.62
	LD3	450	450	400	350	0.792	40.64
	LD4	550	500	450	400	0.798	39.68
	LD5	500	450	400	350	0.801	28.62
	CD1	400	350	300	250	0.820	40.80
	CD2	450	400	350	300	0.892	39.85
0.25%	LD1	650	600	500	450	0.878	36.48
	LD2	550	550	500	400	0.784	38.82
	LD3	500	450	450	400	0.786	40.92
	LD4	600	550	450	400	0.794	41.1
	LD5	500	450	400	400	0.801	42.86
	CD1	500	450	400	350	0.821	40.60
	CD2	500	450	400	350	0.834	39.96

Cont…

Conc.	Sample	Foam volume in cm^3 (time in min.)				Density (gm/cc)	Surface tension (dyne/cm)
		0	5	10	15		
0.5%	LD1	700	600	550	500	0.794	24.65
	LD2	600	550	550	500	0.799	36.62
	LD3	550	450	400	350	0.812	39.45
	LD4	600	600	500	450	0.791	38.23
	LD5	500	500	550	500	0.862	37.45
	CD1	600	550	400	300	0.851	23.63
	CD2	600	450	400	350	0.871	32.21
1%	LD1	750	750	700	700	0.8308	32.59
	LD2	700	700	650	600	0.99	35.18
	LD3	650	650	550	500	0.99	35.68
	LD4	700	650	600	500	0.98	34.73
	LD5	650	600	550	550	0.94	36.57
	CD1	700	650	400	350	0.99	24.62
	CD2	700	600	450	400	0.99	30.21

Abbreviation: - LD-Liquid Detergent, CD-Commercial Detergent

Table 7: Effect of liquid detergents on % detergency with 1% solution

Cloth	Medium for staining	% Detergency by liquid detergent						
		LD1	LD2	LD3	LD4	LD5	CD1	CD2
Cotton	Soil	89.00	87.00	84.00	86.5	86.00	91.20	87.62
	Spinach	85.00	82.50	82.50	82.50	82.19	89.62	90.68
	Tea	62.16	64.86	56.78	70.27	64.89	76.84	77.64
	Coffee	77.14	65.78	76.56	77.32	79.64	74.52	80.00
Polyester	Soil	86.50	84.92	80.62	84.01	84.50	88.12	85.00
	Spinach	85.00	80.12	80.62	81.36	83.19	89.62	67.62
	Tea	66.14	66.66	66.12	74.62	76.23	79.60	62.62
	Coffee	75.14	63.05	69.12	71.65	76.32	82.12	79.62

Cont…

Cloth	Medium for staining	% Detergency by liquid detergent						
		LD1	**LD2**	**LD3**	**LD4**	**LD5**	**CD1**	**CD2**
Terricot	Soil	84.68	83.69	81.74	82.10	81.13	86.65	83.32
	Spinach	83.77	81.62	79.62	81.60	74.32	88.60	84.60
	Tea	69.66	64.92	69.60	81.60	74.32	81.62	66.12
	Coffee	72.62	62.30	66.32	68.89	76.65	80.69	69.54

RESULTS AND DISCUSSION

Table 1 gives composition of selected novel polymers with desired properties. The major ingredients of polymer are coconut oil and linseed oil, while minor ingredient is maleic anhydride. The catalysts used are hydrochloric acid, sodium bisulphite and sodium bisulphate. The time of heating is 5 hr & 30 mintues at 230°C.

The possible chemical reaction is malenized formation by Diels Alder reaction and additions at active methylene group. The physiochemical properties of these polymers are given in Table 2. The color and consistency of the polymer is acceptable for commercial use. The polymers are soluble in xylene: butanol, alcohol and NaOH. The surface tension data indicates significant lowering of surface tension by novel polymers. The HLB value[9] of products indicates it utility as ingredient in detergent compositions.

The prepared malenized oil were neutralized with 30% KOH to get a sample with 8.0 pH. This neutralized sample has been used for detergent formulations, The % detergency and foam height of neutralized polymer are given in Table 3. Neutralized malenized oil has a better detergency for soil removal compared to conventional active materials like acid slurry and alpha olefin sulphonate. Samples of neutralized malenized oil are 10 to 20% superior compared to conventional products.

The compositions of liquid detergents is given in Table 5. The polymer M-1 and M-2 have been used in liquid detergent compositions in the ratio of 10 to 20%.

The samples have foaming characteristics[8] equivalent to commercial sample the reduction in surface tension is also appreciable and comparable to commercial sample. The special features of formulation are freedom from petroleum based actives.

The soiling removing characteristics[11] on different cloths are shown in Table 7. At 1% concentrations for terricot cloths, our samples have detergency of 82 to 86% which is

comparable to commercial liquid detergents. With cotton and polyester cloths the detergency at 1% concentrations is 84 to 90% which is nearer to the results of commercial products.

CONCLUSION

The following conclusions stands confirm in the light of above research

(i) Linseed oil and coconut oil can be modified to get malenized oil with desired acid value, viscosity and HLB value.

(ii) Malenized oil synthesized using linseed oil and coconut oil has huge potential and can be used as substitute petroleum based actives like acid slurry and sodium lauryl sulphate.

(iii) A combination of hydrochloric acid, sodium bisulphate, sodium bisulphite as catalyst give excellent results.

(iv) The final yield of malenized oil is 95-98%.

(v) The higher acid value of malenized oil is helpful in making water thinnable composition. We can neutralize these resins with sodium hydroxide and potassium hydroxide, malenized oil neutralize by potassium hydroxide have been used in various liquid detergents formulations.

(vi) The physiochemical analysis like HLB value, viscosity, clarity and color of polymer strongly indicates its application for liquid detergent compositions.

(vii) The study indicates the possibility of pilot scale and commercial scale production of malenized oil. This malenized oil can be prepared with simple equipment and small scale liquid detergent industry can be made self sufficient to some extent.

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