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Malenised vegetables oils - a substitue for linear alkyl benzene sulphonate and alpha olefienic sulponate for ecofriendly powder detergents

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ABSTRACT

Malenized Linseed oil and Coconut oil suitable for use in Powder 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 Powder detergent mainly based on malenised vegetables oils and Alpha olefin sulphonate has been prepared. In successive compositions acid slurry has been replaced by neutralized malenized linseed oil by 50 to 100% .A comparison of our maleic based detergents with commercial samples shows that maleic treated oils give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 Powder detergents in reasonable and they can be tried on pilot scale and commercial scale production. The special feature of these Powder detergents is freedom from conventional linear alkyl benzene sulphonate and sodium tripoly phosphate so they can be labeled as ecofriendly products for green environment.

Introduction

A number of methods have been suggested for improving the properties of drying oils which involve the separation of the better-drying from the poorer drying components (segregation), the shifting of non-conjugated double bonds to conjugated form (isomerization) and the removal of water to introduce a new double bond (dehydration). There is another method of adding unsaturated compound to the unsaturated part of the oil molecule, thus increasing its complexity and heat reactivity. The compound referred to is Maleic treated or Malenized oil. Maleic anhydride along with phthalic anhydride and can be used for modification and the modified oil is known as malenized oil.

Since the maleic is added near the unsaturation section of the fatty acid radical it retards oxidation slightly so that maleic treated oils do not show greatly increased air-drying properties. However they are definitely faster bodying and have better colour and at equal viscosity and better water resistance in the dried films. Maleic anhydride is a dibasic acid which reacts with both conjugated and isolated double bonds. The possible chemical reactions are addition reaction of Maleic anhydride. When we heat the oil, a part of linolinic acid is converted to9, 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.

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.

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.

Experimental

A) 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 in to 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.

B) 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 200^0C in about half an hour. This temperature was maintained for one hour. The reaction temperature was then raised to 230^0C and reaction was continued steadily for two hours at this temperature. Now steadily reaction temperature was lowered down to 150^0 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.

C) Neutralization of malenised vegetable oil: - 100 gm of Novel copolymer was heated to 70 ^{0}C the calculated amount of KOH was added to novel polymer with constant stirring so as to get slightly alkaline solution of polymer with pH 8.

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Heating schedule for Preparations of Malenized Oils

Initially the heating is done slowly and steadily so that a temperature of 200^0C is attained in about 2 hours this is essential, as maleic anhydride has a tendency to sublime, initially the temperatures is maintained at 200^0C then slowly it is taken to 230^0C.A cooking of 3 hours at this temperatures is essentials to get the desired degree of polymerization and molecular weight. At the end, heating of 30 minutes at 150^0C give a slow and steady growth of polymer. The total time of heating is 5 hours and 30 minutes.

Result and Discussion

1) Formulation of Powder detergents

Malenized vegetables oils based on linseed oil and coconut oil can be successfully used as a replacement of acid slurry in various proportions without adversely affecting the useful properties like surface tension, soil, tea, coffee, spinach stain removing are on par or even better than commercial samples tested simultaneously.The incorption of malenized oils reduce the foam of detergents. This behavior can be used to develop moderate or low foaming detergents which can be save water in cleansing operations.

2) Analysis

The analysis of powder detergent is given. The moisture content of Samples is 3 to 4%.The pH of samples vary from 8.7 to 9.13.Good results are obtained at pH 8.3 to 8.5.The results are comparable to two commercial samples tested simultaneously.

1. The foaming property and foam stability is moderate. These compositions have less foaming compared to commercial samples. Thus at a level 1% the foaming is 50% of commercial samples. However the reduction in surface tension is quite good and appreciable at 1%.
2. The detergency on technically soiled cloths of malenized oil (M-A) is good to excellent for a large number of compositions it is comparable and sometimes better than commercial products tested simultaneously. The detergency for cotton cloths is slightly better than other type of cloths .The detergency of sample PD-1 which is free from acid slurry is good and superior to commercial samples for coffee stain.
3. The tea stain removing is excellent and comparable to Commercial samples. Coffee stain removal is good for large no of samples with few exceptions.
4. The spinach stain removal is good but slightly lower than commercial samples CD1and CD2.
5. M-A for soil and other stain removing properties are good comparable to commercial but for spinach stain removal appears to be best.
6. There is a global trend of using foamless detergents throughout the world our samples are giving moderate foam so there will be certainly saving of water to some extent which is required from water consumption view point.

Results of Powder Detergents Based on Malenized Oil

The special of these powder detergents formulations are as follows

1. The formulations are based on soft acid slurry, sodium lauryl sulphate and malenized oil samples, the highest amount of acid slurry used is 6.0% in first formulation. In successive compositions the soft acid slurry has been reduced from 6 to 0% while malenized oil has been used progressive from 1.7 to 8.5%.Thus, the final sample is totally free from acid slurry.
2. A constant proportions of sodium lauryl sulphate (15%), sodium carbonate (12%), sodium sulphate (22%) urea and zelolite powder has been used in all formulations.
3. All the literature suggests that salt should not be used more than 5% .However, we have used 25% salts.The use of salt has double advantage it reduces the cost of compositions, simultaneously it helps in breaking emulsion of oily soily materials. It has no negative impact on detergency and properties.
4. The samples are free from sodium tripolyphosphates so no river or lake pollution can be there. The content of sodium carbonate is just moderate (12%) Many of the conventional compositions use from 20 to 40% sodium carbonate. These higher proportions are irrating to hands and harsh to cloths particularly dyed cloths.

Conclusion

The following conclusions stand confirmed in the light of above experimental work

1. Malenized oils based on vegetables renewable sources like coconut oil and linseed oil can be successfully introduced in Powder detergent composition from 2 to12% without adversely affecting the foam, surface tension, cleaning and stain removing capacity.
2. Acid slurry which is of petroleum origin can be replaced Malenized oils in any desired Proportions by our without sacrificing technical and cleaning properties.
3. The samples are ecofriendly as we are not using any sodium tripolyphosphates and acid slurry. The other ingredients are of harmless vegetables origin.
4. Various Stains like Soil, Tea, Coffee and Spinach can be successfully removed by our compositions using Malenized oils. In some instantances the stain removing is better or superior then the commercial samples which were tested simultaneously.
5. The samples prepared with a pH having eight and moisture content 4-5% give excellent foaming, reduction in surface tension and cleaning properties. Samples based on Malenized oils are on par or some times better than commercial samples.

Table No.1:-Composition of Novel Malenized Oil (%by weight)

Ingredient	Batch No.1 (M-A)
Linseed oil	35
Maleic anhydride	10
Coconut Oil	50
Benzoic Acid	01
Oxalic Acid	02
Citric Acid	02

Catalyst used: 1.5% sodium Bisulphate, 0.5% ,sodium bisulphite and 1% Hydrochloric acid on Weight of total mass.

Table No.2:-Physico-Chemical Properties of Malenized Oil

Sr.No.	Test	M1	M2
1	Acid value	33.66	28.98
2	Viscosity (By ford Cup No.4 in sec.)	260	290
3	Color	Brown	Brown
4	Solubility 1)Alcohol 2)50%NaOH 3)Xylene:butanol	Soluble Soluble Soluble	Soluble Soluble Soluble
5	pH value	2.51	2.69
6	Molecular weight	3091	3225
7	H.L.B. ratio	15.0	16.9

Table No.3:- % Detergencyof Original Polymer

Conc.	M1	M2	Acid Slurry	Alpha Olefin Sulponate
0.1	78	71	62.00	58.20
0.25	81	77	66.50	63.60
0.5	84	79	70.85	69.80
1.0	86	83	85.00	83.33

Table No 4:-Variation In % Detergency With Ph

BATCHES	PH VALUES			
	Original	PH-8	PH-10	PH-11
M1	86	86	81	77
M2	83	88	71	64

Note-For testing of detergency, malenized oil was neutralized with 50%KOH to get a pH of 8 .This solution was used for measurement of stain removal and foam height.

Table No 5: Compositions of Powder Detergent based on Malenized oil

Sr. No.	Ingredients	% composition by weight					
		PD1	PD2	PD3	PD4	PD5	PD6
1	Neutralized Acid slurry (75% soild)	7.5	6.0	4.5	3.0	1.5	0.00
2	Sodium Lauryl Sulphate	5.0	5.0	5.0	5.0	5.0	5.0
3	Sodium Carbonate	12.0	12.0	12.0	12.0	12.0	12.0
4	Sodium Sulphate	22.0	22.0	22.0	22.0	22.0	22.0
5	Urea	3.5	3.5	3.5	3.5	3.5	3.5
6	Salt	25.0	25.0	25.0	25.0	25.0	25.0
7	Dolomite	15.0	15.0	15.0	15.0	15.0	15.0
8	Zeolite powder	3.0	3.0	3.0	3.0	3.0	3.0
9	Brighnter	3.0	3.0	3.0	3.0	3.0	3.0
10	Neutralized Malenized oil (M-A) (80%soild)	---	1.8	3.6	5.4	7.2	9.0
11	Distilled water	4.0	3.7	3.4	3.1	2.8	2.5

Table No: 6.Analysis of Powder detergents

Sr.No.	Sample	%Solid	pH
1	PD1	92.25	8.7
2	PD2	93.54	8.39
3	PD3	92.98	8.45
4	PD4	93.54	8.32
5	PD5	94.21	9.13
6	PD6	93.65	8.41
7	CD1	96.21	8.59
8	CD2	95.40	8.34

Table No.7: Physiochemical properties of Powder detergents Based on Malenized oil (M-A)

Conc.	Sample	Foam volume in CM^3 (time in min.)				Surface Tension (dyne/cm)
		0	5	10	15	
1%	PD1	300	250	250	200	35.2145
	PD2	250	200	150	150	34.5623
	PD3	150	100	100	100	34.1287
	PD4	150	150	100	100	33.0154
	PD5	150	100	100	100	32.4501
	PD6	150	150	100	100	32.5648
	CD1	300	250	200	150	30.2541
	CD2	250	200	200	150	30.3581

Abbreviation: - PD-Liquid Detergent, CD1 and CD2 are Commercial Detergent samples.
Comment-The foam Height and foam stability is less and comparable to commercial samlpes.

Table No.7:- Effect of Powder detergents on% Detergency with 1%solution

Cloth	Medium for Staining		% Detergency by liquid detergent						
		PD1	PD2	PD3	PD4	PD5	PD6	CD1	CD2
Cotton	Soil	89.00	87.00	84.00	86.5	86.00	87.52	91.20	87.62
	Spinach	85.00	82.50	82.50	82.50	82.19	83.62	89.62	90.68
	Tea	62.16	64.86	56.78	70.27	64.89	68.21	76.84	77.64
	Coffee	77.14	65.78	76.56	77.32	79.64	82.1	74.52	80.00
Polyester	Soil	86.50	84.92	80.62	84.01	84.50	85.63	88.12	85.00
	Spinach	85.00	80.12	80.62	81.36	83.19	85.42	89.62	67.62
	Tea	66.14	66.66	66.12	74.62	76.23	78.96	79.60	62.62
	Coffee	75.14	63.05	69.12	71.65	76.32	78.20	82.12	79.62
Terricot	Soil	84.68	83.69	81.74	82.10	81.13	83.62	86.65	83.32
	Spinach	83.77	81.62	79.62	81.60	74.32	77.85	88.60	84.60
	Tea	69.66	64.92	69.60	81.60	74.32	77.20	81.62	66.12
	Coffee	72.62	62.30	66.32	68.89	76.65	79.21	80.69	69.54

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