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Some resin based ecofriendly liquid detergents

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In this study, efforts were made to replace from detergent the conventional active matter, linear alkyl benzene sulphonate (LABS) formulation by polymeric surfactant (alkyd resin). An ecofriendly alkyd resin polymer based on soybean oil and rosin was synthesized and used with sodium lauryl sulphate (SLS) instead of LABS for detergent formulation. Based on surface tension, detergency and foam volume, prepared compositions are on par or sometimes better than commercial samples even at very low (0.5%) liquid detergent. The proposed compositions can be easily prepared in existing alkyd resin manufacturing plant. An alternative production line was suggested for existing alkyd resin plants in paint industry.

Keywords: Alkyd resin, Polymeric surfactant, Liquid detergent

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Introduction

India has a very vast capacity of manufacturing alkyd resins, which are used in surface coating industries. The per capita consumption of detergent is higher than surface coating (paint industry), therefore, alkyd resin plants can produce alkyds in the same set up without much investment. The use of polymeric additives in detergents is common since last 25 years. The important characteristics of a polymer are adsorption on fabrics, Ca and Mg sesquesterization, $CaCO_3$ inhibition, fabrics anti incrustation and soil disperancy and removal[1]. Polycarboxylated polymers like styrene maleic co-polymer and acrylic maleic co-polymer have been successfully used as detergent additives. Authors have successfully used starch and sorbitol based polymers in liquid and powder detergents[2-5]. The reduction and removal of polyphosphates for getting ecofriendly detergents are only possible because of polymeric surfactants. In earlier work, polymeric surfactant was used only as an additive while authors used alkyd resin as a total substitute of linear alkyl benzene sulphonate (LABS) successfully. Rosin, a major ingredient of alkyd resin polymeric surfactant is a surface-active agent[6].

This study presents total replacement of LABS with polymeric surfactant, utilizes the surfactant based on polymer for detergency, and suggests an alternative product as a diversification for existing alkyd resin plants without much additional investment. The polymeric surfactant based on vegetable oil and rosin will be certainly biodegradable and ecofriendly as they are from renewable vegetable sources.

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Experimental Details

Materials

Soybean oil used was of industrial grade (Gwalior Oil Ltd, Gwalior); Rosin N.grade (BIS); benzoic acid, phthalic anhydride, sodium bisulphate, sodium bisulphite, maleic anhydride, EDTA, polyvinyl alcohol, sodium lauryl sulphate, sodium lauryl ether sulphate, NaOH; glycerol, xylene, 1-butanol and sorbitol (S.D.Fine Chem. India.); and urea (commercial grade).

Synthesis of Alkyd Resin[7]

Alkyd resin contained: soybean oil, 19.0; glycerol, 17.9; rosin, 42.6; maleic anhydride, 2.8; benzoic acid, 2.8; sodium bisulphite, 0.5; sodium bisulphate, 1.5; and phthalic anhydride, 15.0%. The mixture was charged and reacted in a standard glass reactor (2 l) fitted with a stirrer, water condenser and temperature control arrangement. Xylene and 1- butanol (3:1) were used as solvent. Details of heating schedule and order of addition of reactants are given in Table 1. After completion of reaction, solvent was removed from product by vacuum evaporation at 200 mmHg (1 mmHg=133.322 Pa).

Neutralization and Water Dispersion of Alkyd Resin[5]

In a beaker, resultant alkyd resin (100 g) was melted and then cooled to 80°C. Required amount of 30% aq. NaOH solution was added to alkyd resin with constant stirring (130-140 rpm/h) so as to get the slightly alkaline solution of polymer with pH 7.5.

Manufacture Analysis and Testing of Liquid Detergent[8]

Liquid detergents (5 samples) were prepared using different concentrations of alkyd resin with sodium lauryl sulphate (SLS), sodium lauryl ether sulphate (SLES), PVA, sorbitol, EDTA and urea in a beaker (1 l) and stirring was continued for 30 min (Table 2). A clear solution of liquid detergent was obtained. The surface tension of liquid detergents was measured using stalagnometer. Foam was measured by using mechanical agitation in a closed vessel method.

Detergency Test

Soil Medium

In pestal mortal, coconut oil (35.8%) was added to a mixture of carbon black (28.4%), lauric acid (17.9%) and mineral oil (17.9%) slowly to form thick paste. The components were ground in pestle mortal for 1-2 h to get fine grinding and smooth filling. The paste (2g) was mixed well with carbon tetrachloride (500ml) and used for soiling of cloths. Spinach medium (spinach juice) was prepared by squeezing spinach leaves between rubber rollers.

Table 1 — Heating schedule and order of addition of reactants.

Order of addition of reactant	Time of heating h
Stage A	
1) Soybean oil, glycerol, rosin, maleic anhydride, benzoic acid, sodium bisulphite, sodium bisulphate.	1
2) Heat at 160°C	2
3) Heat at 230°C	
4) Cool down slowly to 80°C	
Stage B	
5) Add 5% solvent* and phthalic anhydride	
6) Heat at 220°C	3
7) Heat at 200°C	1
8) Heat at 190°C	2
9) Cool to 80°C and remove the product	

*Solvent- Xylene: 1- Butanol (3:1)

Fabric Soiling

The white tericot, cotton fabrics (10 cm x 10 cm) were prepared and dipped in the above mediums for 10 min. These soiled fabrics were kept for drying in open-air for 2 days.

Washing

The washing was done using Terg – O – Tometer as follows: speed, 100 rpm; washing solution, 1000 ml; washing time, 15 min; rinsing time, 10 min; temp, 50°C; and water hardness, 250 ppm. Different concentrations (0.1, 0.25, 0.5 & 1.0%) of liquid detergent were used for washing. Same concentrations were tried with commercial liquid detergent. After washing, the detergency (%) was calculated using Lambert & Sanders formula[9].

$$\% \text{ Detergency} = \frac{(Rw-Rs)\ x100}{(Ro-Rs)}$$

where, *Rw*, *Rs* and *Ro* are the reflectance measured on washed fabrics, soiled fabrics (before washing), and unsoiled fabrics respectively. The reflectance was measured with an Elrepho reflection photometer with filter R-46 against an MgO-standard.

Results and Discussion

Alkyd resin polymeric compositions of high acid value were prepared. The amount of rosin in polymer was quite high (42 %). The amount of soybean oil was maintained at lower level (19 %). Normally, reducing the oil below 30 percent, it is very difficult to prepare alkyd resin polymer due to gelation. But authors prepared a short oil rosinated alkyd resin polymer (oil length, 19 %). It is possible due to use of

Table 2 — Composition of liquid detergents (% wt)

Ingredients	LD_1	LD_2	LD_3	LD_4	LD_5
SLS	7.0000	6.0000	5.0000	4.0000	3.0000
SLES (100% solids)	5.5696	5.5696	5.5696	5.5696	5.5696
Alkyd resin	1.0000	2.0000	3.0000	4.0000	5.0000
Sorbitol (100% solids)	5.6000	5.6000	5.6000	5.6000	5.6000
Urea	3.0000	3.0000	3.0000	3.0000	3.0000
EDTA.	0.5000	0.5000	0.5000	0.5000	0.5000
Polyvinyl alcohol	1.0000	1.0000	1.0000	1.0000	1.0000
Water	76.0908	75.8312	75.6116	75.3305	75.1324
NaOH	0.2396	0.4792	0.7188	0.9999	1.1980

chain stoppers benzoic acid, rosin and soybean oil. Rosin helps in smooth progress of polymerization without gelation and water dispercibility. Liquid detergents based on different combinations of SLS with alkyd resin were formulated (Table 2). The formulations also contained usual ingredients such as polyvinyl alcohol and urea. SLES was used as foaming agent. EDTA was used as water softener. All the prepared compositions were evaluated for foam volume, surface tension and detergency percentage and compared with standard commercial samples (Tables 3-8). All the tests were conducted as per Indian Standard[10,11]. All the prepared samples are comparable with commercial sample in respect of surface tension except LD_5, which needs to be corrected. Samples LD_5 gives a lower foam volume compared to commercial sample while LD_1, LD_2, LD_3, LD_4 give higher foam volume. As the percentage of alkyd resin is increased in the composition of liquid detergents, foaming characteristics are suppressed and this property of alkyd resin can be used to develop a foamless detergent for washing machine. The detergency percentage data of prepared samples is in good agreement with commercial sample except LD_5.

The conventional commercial detergents contain LABS as their active ingredients. It is a petroleum

Table 3 — Foam volume, surface tension at 0.1% conc. of detergent in water

Samples	Foam volume (ml) min				Surface tension dyne/cm
	0	5	10	15	
LD_1	152	152	152	145	45.9210
LD_2	148	145	142	138	45.6210
LD_3	135	132	128	125	45.0210
LD_4	130	130	125	120	45.0904
LD_5	115	115	110	105	47.6215
Commercial liquid detergent	132	130	126	126	45.5720

Table 4 — Foam volume, surface tension at 0.25% conc. of detergent in water

Samples	Foam volume (ml) min				Surface tension dyne/cm
	0	5	10	15	
LD_1	200	200	195	187	35.6968
LD_2	195	191	187	182	35.0956
LD_3	185	182	181	180	35.9423
LD_4	179	179	175	170	36.9447
LD_5	156	154	150	150	42.4276
Commercial liquid detergent	168	168	160	157	39.2835

Table 5—Foam volume, Surface tension at 0.5% conc. of detergent in water

Samples	Foam volume (ml) min				Surface tension dyne/cm
	0	5	10	15	
LD_1	400	400	390	390	31.5001
LD_2	310	307	303	297	30.0218
LD_3	300	300	295	291	30.4218
LD_4	250	250	245	240	29.6201
LD_5	200	200	195	190	37.3870
Commercial liquid detergent	350	340	330	330	33.9769

Table 6—Foam volume, surface tension at 1.0% conc. of detergent in water

Samples	Foam volume (ml) min				Surface tension dyne/cm
	0	5	10	15	
LD_1	605	600	595	590	28.5088
LD_2	570	570	565	565	29.9331
LD_3	480	475	475	470	28.6188
LD_4	430	425	420	420	27.1633
LD_5	280	275	270	265	30.7420
Commercial liquid detergent	500	490	480	480	28.8878

Table 7—Spinach stain on terricot, cotton fabrics (% detergency)

Samples	Conc. %	Tericot		Cotton	
		Rw	Detergency %	Rw	Detergency %
LD_1	0.1	68.4	68.71	69.4	64.88
	0.25	69.6	75.41	72.0	72.61
	0.5	70.9	82.68	75.0	81.54
	1.0	73.0	94.41	78.0	90.47
LD_2	0.1	68.5	69.27	70.0	86.66
	0.25	70.2	78.77	72.7	74.70
	0.5	71.1	83.79	76.5	86.01
	1.0	72.5	91.62	78.6	92.26
LD_3	0.1	68.1	67.03	70.4	67.85
	0.25	70.4	79.88	73.1	75.89
	0.5	71.6	86.59	77.3	88.39
	1.0	72.9	93.85	77.6	89.28
LD_4	0.1	69.3	73.74	70.8	69.04
	0.25	71.4	85.47	75.4	82.71
	0.5	72.4	91.05	77.7	89.58
	1.0	73.2	95.53	78.9	93.15
LD_5	0.1	67.9	65.92	67.2	58.33
	0.25	69.7	75.97	70.9	69.34
	0.5	70.8	82.12	73.5	77.03
	1.0	72.0	88.82	75.8	83.92
Commercial detergent	0.1	68.8	70.94	69.9	66.36
	0.25	69.9	77.09	72.8	75.00
	0.5	71.4	85.47	75.9	84.22
	1.0	72.8	93.29	78.3	91.19

Ro (Reflectance on unstained tericot) = 74.0, Rs (Reflectance on stained tericot) =56.1,
Ro (Reflectance on unstained cotton) = 81.2, Rs (Reflectance on stained cotton) =47.6,
Rw = Reflectance on washed fabrics

Table 8 — Soil solution on Terri cot, cotton fabrics (% detergency)

Samples	Conc. %	Tericot		Cotton	
		Rw	Detergency %	Rw	Detergency %
LD_1	0.1	56.4	66.28	58.7	61.20
	0.25	60.7	74.52	63.4	69.31
	0.5	67.5	87.54	69.9	80.51
	1.0	69.9	92.14	75.3	89.82
LD_2	0.1	64.3	81.41	58.8	61.37
	0.25	66.6	85.82	63.3	72.58
	0.5	67.5	87.54	73.1	86.03
	1.0	69.7	91.76	74.9	89.13
LD_3	0.1	57.3	68.00	62.4	67.58
	0.25	61.1	75.28	65.4	72.75
	0.5	67.9	88.31	73.0	85.86
	1.0	69.5	91.37	75.7	90.51
LD_4	0.1	57.8	68.96	62.8	68.27
	0.25	63.5	79.88	67.7	76.89
	0.5	67.9	88.31	73.4	86.55
	1.0	70.0	92.33	75.2	89.55
LD_5	0.1	54.5	62.64	56.2	56.89
	0.25	59.4	72.03	71.4	65.00
	0.5	64.8	82.37	72.4	78.79
	1.0	68.0	88.50	71.3	82.93
Commercial Detergent	0.1	56.9	67.24	60.2	63.79
	0.25	62.9	78.31	65.8	73.44
	0.5	67.9	86.34	72.1	84.31
	1.0	69.4	91.18	73.7	87.06

Ro (Reflectance on unstained tericot)= 74.0, Rs (Reflectance on stained tericot) =21.8,
Ro (Reflectance on unstained cotton) = 81.2, Rs (Reflectance on stained cotton) =23.2,
Rw = Reflectance on washed fabrics.

product and causes environmental problems. Here authors have tried total replacement of LABS by alkyd resin polymer and SLS (prepared from coconut oil), all are vegetable in origin hence, authors claim that their formulation of detergents are ecofriendly as compared to commercial one, which are synthetic and petroleum in origin. In experimental liquid detergents, active matter is less (8 %) than other available detergents (10–15%). The manufacturing cost of experimental detergent is Rs 30 per kg, which is quite encouraging.

Conclusions

Authors synthesized alkyd resin, a polymeric surfactant, to assess the feasibility of using them for liquid detergent formulation in association with SLS instead of using LABS. Polymeric surfactants had demonstrated their utility as an active ingredient of detergent. All the prepared compositions of liquid detergents have equivalent performance compared to commercial one with respect to surface tension and detergency percentage except LD_5. Foaming property gets suppressed with increase in amount of polymer. Main ingredients of polymer liquid detergents are natural in origin hence, present product is economic and ecofriendly. The present research work will open up a new horizon of using alkyd resin polymers in surfactant.

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