Int. J. Chem. Sci.: 9(2), 2011, 825-835
ISSN 0972-768X
www.sadgurupublications.com

NATURLY SYNTHESISED ECOFRIEDLY CARBOHYDRATE BASED POLYMERIC SURFACTANTS FOR LIQUID DETERGENTS AND POWDER DETERGENTS

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ABSTRACT

In last five decades there is a common trend to use petroleum products as active and useful ingredients in commercial products like liquid and powder detergents, paints, printing inks, cosmetics and textiles auxiliaries. Commercial detergent powder use linear alkyl benzene sulphonate in the range of 15-20%. There is a need to synthesize novel product based on vegetable origins which are ecofriendly and biodegradable. Efforts are necessary to substitute this petroleum based products on novel polymers.

The present research work is aimed at developing a polymeric surfactants based on sorbitol, maleic anhydride, phthalic anhydride, oxalic acid, citric acid and starch as the polymeric surfactant is based on sorbitol and starch which will have biodegradable characteristics. It is used in powder detergent and liquid detergent formulation as partial substitute for LABS and AOS. In our laboratory we are working from last two decades on novel polymeric surfactants mainly based on vegetable sources like starch, sorbitol etc. We have developed novel polymers which can be used in wall finishes, enamels, printing inks and liquid and powder detergents. We are trying to formulate detergents consisting dolomite, silicate with minimum amount of STPP.

Key words: Ecofriendly, Carbohydrate, Polymeric surfactant, Liquid and Powder detergents.

INTRODUCTION

A word Globalization itself shows competition, fast communication, advancement in research and development and many more. The globalization has given a world a beautiful scenario of success and fast growth but on the other hand it has also lead to fast consumption

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of our natural resources to a very large extent leaving a scarcity to be full filled. This has widely diversified the research and development activities all over the world to work for modifying current natural resources. As globalization and increased world population is leading world towards extinction of non renewable source mainly petroleum. This scarcity can only be full filled by modifying renewable sources to such a level that it can match up in its properties, quality and other properties with non renewable source.

Several industries like paint, detergents, inks and germicidal are mainly dependant on petroleum products, for example acrylic resin, various volatile organic solvents in paint industry. Alkyl resin one of the main ingredient of paint industry has 50% or more percentage of phthalic anhydride and maleic anhydride which are derived from petroleum origin. Organic solvents like toluene, xylene and benzene are petroleum origin and used in paint industry. Likewise linear Alkyl Benzene Sulphonate (LSBS) is used to a very large extent in detergent industry is also the example of use of petroleum products. There are many more examples which ultimately show the extensive usage of petroleum products which has developed a global pressure on petroleum products.

The present generation of surfactants is based on linear alkyl benzene sulphonate or similar materials, which are obtain from crude petroleum. The price of crude petroleum is quite high; the stock of crude petroleum is soaring year after year so we must develop renewable vegetative base alternatives for these conventional petroleum based surfactants.

Every industry today is searching for alternative renewable resources of vegetable origin as the petroleum products are souring in price and availability. Thus biodegradable plastics, eco-friendly surfactants and water thinnable paints are the key words in global search for alternative raw material. In the last three decades the awareness and research on eco-friendly products has increased at a very fast pace.

Objectives

The present work has following objectives -

(i) The basic idea of this research work is to obtain the optimum ratio of the LABS to carbohydrate based polymers, which will give the excellent technical performance. Thus we are trying to formulate ecofriendly detergent based on renewable vegetable source like sorbitol, starch, maleic anhydride, phthalic anhydride, which are having desired properties useful for products like liquid detergent, powder detergent and detergent cakes.

(ii) These polymers will be analyzed for various physicochemical properties such as HLB, viscosity, molecular weight, Sap. value, pH, acid value etc. and spectral properties like IR and NMR will also be studied.

(iii) A combination of conventional active materials like sodium lauryl sulphonate, sodium lauryl ether sulphate, alpha olefin sulphonate, along with novel polymers has been used in a synergistic manner to developed detergents (LD & PD) of practical value. In this way the present work is aimed at developing ecofriendly, cost effective and technically superior powder detergents, liquid detergents and detergent cake based on novel carbohydrate polymers.

EXPERIMENTAL

Synthesis of carbohydrate polymers

The polymer based on carbohydrate dates back to as early as the 1930s. Reppe (1930) was the first to synthesize vinyl saccharide monomer. He synthesized ether from glucose and fructose by alkali catalyzed addition of protected sugars to acetylene.

The esters of carbohydrates are completely soluble in water and found to be suitable in the detergent formulations. The detergent made out of acid slurry cause harm aquatic flora and fauna. Acid slurry has the petroleum origin. The detergents of petroleum origin are responsible for river foaming and eutrification. By using biodegradable polymers in detergent formulation the above mentioned problems of water pollution can be minimized to greater extent.

The polymers containing carbohydrates are potentially processable and biodegradable and biocompatible polymers. The present research work encompasses the polymer synthesis from carbohydrates, starch, maleic anhydride and phthalic anhydride using water as solvent. Sodium bisulphate and sodium bisulphate used as catalyst in order to formulate the biodegradable detergents.

Surfactants can be produced from starch in combination with fatty acids. Products of these type have been known for as long as other “Synthetic” surfactants formed from petrochemical –derived material. There has been a recent trends towards surfactant based on renewable sources. This trends has been supported by several commercial plant opened by cognis (formally henkle) the driving force behind the trend is the number of benefit gained by starch based surfactants. Desirable properties of these surfactants in addition to being produced from renewable sources are that they are readily biodegradable, they have low

toxicity, they are produced from and degraded into materials of low toxicity, they are mild on the eyes and skin and some can perform synergistically with other surfactants. About 150000 tons of starch derived surfactants are produced annually world wide.

Table 1: Data collection of all batches and their analysis

Name of compounds	Batch B1	Batch B2	Batch B3
Sorbitol	55	45	40
Maleic anhydride	5	5	5
Phthalic anhydride	5	5	5
Maize starch	25	35	40
Oxalic acid	5	5	5
Citric acid	5	5	5

Table 2: Solvent & catalyst used

Catalyst	Batch B1	Batch B2	Batch B3
Sodium bisulphate	1.5	1.5	1.5
Sodium bisulphate	0.5	0.5	0.5
Tween 80/20	-	-	-
HCL	-	-	-
Triethanolamine	-	-	-

Table 3: Batch period-5 hrs at 120^{o}C

Heating period	Batch B1	Batch B2	Batch B3
After 1/2 hr	80°C	70°C	70°C
After 1 hr	100°C	100°C	80°C
After 1.5 hr	110°C	110°C	100°C
After 2 hr	120°C	120°C	110°C

Cont…

Heating period	Batch B1	Batch B2	Batch B3
After 2.5 hr	120°C	120°C	120°C
After 3 hr	120°C	120°C	120°C
After 3.5 hr	120°C	120°C	120°C
After 4 hr	120°C	120°C	120°C
After 4.5 hr	120°C	120°C	120°C
After 5 hr	120°C	120°C	120°C

Table 4: % Yield & batch size

	Batch B1	Batch B2	Batch B3
Yield	93.2	90.0	96.8
Batch size (kg)	1	1	1

Table 5: Analysis

Test	Batch B1	Batch B2	Batch B3
% solid	69.40	69.49	73.93
Acid value	19.20	31.75	22.38
Viscosity	223	374	563
Color	Pinkish	Pinkish	Pinkish
Consistency	Thick	Thick	Thick
Solubility	Water	Water	Water
pH value	4.31	4.08	3.80
Molecular weight	4037.24	4092.28	5417.51
H.L.B. ratio	15.6	15.2	15.0
Saponification value	194.88	213.36	224.56
Ester value	175.68	181.61	202.18

Table 6: Detergency

Medium	Batch B1	Batch B2	Batch B3
Soil	90.90	90.90	95.45
Tea	91.89	86.48	83.7
Coffee	88.57	85.71	74.28
Palak	80	87.5	87.5

Table 7: Detergency based on pH value (soil)

Batches	pH Values			
	Original	pH-8	pH-10	pH-11
B1	90.90	87.23	86.09	86.14
B2	90.90	78.52	77.89	77.89
B3	95.45	74.11	74.01	75.23

Table 8: Heating schedule of novel alkyd polymer (B9) (% by weight)

Procedure: Total charge - 1.0 Kg (Total time of Heating: 3 hrs.)

Sorbitol + maleic anhydride + phthalic anhydride + oxalic acid + citric acid

↓

Mixed all ingredient add to the reactor

↓ Heat at 120ºC for 1Hrs

Add phthalic anhydride by lowering down temperature to 100ºC

↓ Heat at 120ºC for 1Hrs

Maintain temperature for another 1 hr. at 120ºC

↓ Cool at 60ºC

Thin down the resin with

RESULTS AND DISCUSSION

Several experiments were performed to get desired polymer of low acid value, desired molecular weight and pale color. Four polymers with desire characteristics are reported in Table 1. Major ingredient was sorbitol (47-58%) and sugar solution (28-20%).

The higher proportion of sugar result in charring so the limit to which sugar can be tolerated is found to be 28-30%. A small amount of starch power has been used in composition B1 and B3.

A variety of catalyst have been tried which include hydrochloric acid, tween 80, sodium bisulphite and sodium bisulphate. Hydrochloric acid appear to give desirable result.

The preliminary physicochemical analysis is given in Table 3. The acid values are quiet low in the range of 4-12. This indicates esterification reaction between acidic group of phthalic & maleic anhydride and OH group of starch, sorbitol and sugar. The cooking schedule and composition is given in Table 3.

Table 3 gives compositions, cooking schedule and order of addition of reaction the compounds giving OH groups are sorbitol, sugar and starch while component phthalic anhydride and maleic anhydride gives acid groups. It is an esterification reaction the other possible chemical reaction is etherification between two OH groups to give a epoxy group. The physicochemical properties are given in Table 5. The acid value is very low in the range of 4-12 this indicate that acid group have reacted almost completely with alcohol group to form esters. All the samples are highly soluble in water, alcohol, and sodium hydroxide. There is a significant lowering of surface tension.

Table 9: Powder detergent based on these polymers

Name of components (in %)	PD1	PD2	PD3	PD4
Polymer	10	0	2.5	5
Sodium carbonate	30	35	35	35
Sodium lauryl sulphate	5	5	5	5
Alpha olephnic sulphonate	3	3	3	3
Oxalic acid (paste with sorbitol)	1	1	1	1
Robin blue (paste with sorbitol)	0.5	0.5	0.5	0.5
Sodium sulphate	15	20	18.5	15
Salt	5	5	5	5
Dolamite	30	30	30	30

Table 10: Analysis of powder detergent and commercial detergents

Conc.	Samples	Foam volume in cm^3 (time in min.)				Density	Surface tension
0.1%	PD1	600	600	650	650	1.198	49.67
	PD2	650	650	600	550	1.231	50.21
	PD3	680	650	650	600	1.214	49.57
	PD4	700	700	700	650	1.245	49.55
	CD1	700	700	650	650	1.214	49.95
	CD2	650	650	650	650	1.231	49.26
0.25%	PD1	650	650	600	600	1.205	50.239
	PD2	700	650	650	600	1.201	50.63
	PD3	700	700	700	650	1.212	50.64
	PD4	700	650	650	600	1.211	50.28
	CD1	700	650	650	650	1.223	50.24
	CD2	700	700	650	650	1.245	50.21
0.5%	PD1	800	750	750	700	1.209	49.12
	PD2	800	800	800	750	1.195	49.23
	PD3	800	750	700	700	1.119	48.59
	PD4	800	750	750	700	1.203	48.79
	CD1	800	800	800	750	1.206	48.25
	CD2	800	750	750	700	1.201	48.12
1%	PD1	900	900	850	850	1.214	50.11
	PD2	950	900	900	850	1.212	45.22
	PD3	900	850	850	800	1.211	51.23
	PD4	950	950	900	900	1.212	50.26
	CD1	900	900	850	850	1.213	50.69
	CD2	900	850	850	850	2.215	50.35

Table 11: Liquid detergent based on these polymers

Name of components	LD1	LD2	LD3
Sles	10	20	20
AOS	10	10	10
Urea	3	3	3
Sorbitol	10	20	20
EDTA	0.25	0.25	-
SLS	5	5	5
Sodium sulphate	5	5	-
Oxalic acid (paste with sorbitol)	2	-	-
PVA (10%)	-	5	5
Polymer-b-3	10	10	10
Water	44.5	22.75	27

Table 12: Physicochemical properties of liquid & comm. liquid detergent

Conc.	Samples	Foam volume in cm^3 (time in min.)				Density	Surface tension
0.1%	PD1	700	700	700	650	1.159	50.33
	PD2	750	750	700	700	1.156	50.32
	PD3	700	650	650	650	1.214	50.65
	CD1	700	700	650	650	1.255	50.29
	CD2	750	700	700	650	1.165	50.24
0.25%	PD1	750	750	700	650	1.196	50.56
	PD2	750	750	700	700	1.167	50.48
	PD3	750	700	700	650	1.199	50.26
	CD1	750	750	700	650	1.245	50.47
	CD2	750	750	700	700	1.231	50.34

Cont…

Conc.	Samples	Foam volume in cm^3 (time in min.)				Density	Surface tension
	PD1	800	800	750	750	1.214	50.29
	PD2	800	750	750	750	1.213	49.95
0.5%	PD3	850	850	800	750	1.211	49.99
	CD1	850	850	800	750	1.240	50.25
	CD2	850	850	800	750	1.223	50.28
	PD1	900	850	850	850	1.226	50.21
	PD2	850	850	850	800	1.229	50.34
1%	PD3	900	850	850	850	1.204	50.29
	CD1	900	850	850	800	1.218	50.37
	CD2	900	850	850	850	1.213	50.28

Five detergent samples have been prepared based on novel polymer B3 developed in the synthesis. Sample PD1 is based on acid slurry while PD2 and PD3 are based on alpha olefin sulphonate and special whitener based on sorbitol and titanium dioxide has been used. This imparts additional whitening effect on the cloth samples PD4, used 10-15% of polymer B3. The special features of PD4 compositions are their freedom from acid slurry or alpha olefin sulphonate vegetable product like sodium laurylsulphate. Novel polymer have been used instead of petroleum products. Amount of sodium tripolyphosphate is kept at minimum 3-5% the analysis of sample is given in Table 5. On an average the moisture content of samples is between 9-12% while pH varies between 8-9. The foaming characteristics and surface tension are given in Table 10 and 12. The sample PD4 based on 10-15% novel polymer shows excellent foaming comparable to commercial sample as indicated in Table 10. The surface tension data also indicate significant lowering of surface tension in samples based on novel polymers. The results are comparable to commercial samples CD1 and CD2 tested simultaneously. Detergency testing carried out on detergents based on novel polymers and commercial products like Surf Excel.

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Revised : 01.03.2011 *Accepted : 02.03.2011*