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Novel Polymeric Surfactants Based on Oxalic Acid and Citric Acid for Detergents

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Abstract

Polymeric surfactant based on sorbitol, maize starch, acids and anhydrides have been synthesized and used successfully in detergent compositions. In the present piece of research work a small quantity of oxalic acid and citric acid along with major quantity of maize starch and sugar solution has been used in synthesis of polymer. The overall idea is to develop a polymeric surfactant using higher quantity of maize starch and substantial quantity of sugar along with oxalic acid and citric acid. These polymers may be ecofriendly are based on vegetable products. The synthesized polymers have been analyzed for physicochemical characteristics like acid value, saponification value, HLB ratio and cleaning efficiency .Selected novel polymeric surfactants based on these observations have been used in the preparation of powder detergent and liquid detergent. The acid slurry and Alpha Olefin Sulphonate based on crude petroleum have been successfully replaced by 50-70% by these novel ecofriendly polymers. The preparation of these polymers is simple and they can be recommended for commercial use. These novel polymers are comparable to commercial active ingredients and suitable for like commercial production. The novel polymers and detergents compositions can be taken up on pilot and industrial scale as they are ecofriendly and commercially and technically comparable to conventional products.

Keywords: Novel polymers, carbohydrate polymers, starch-sorbitol-sugar based polymers.

Introduction

The advent of polymers represents one of the important industrial revolutions of the 21st century. The polymers containing carbohydrates are unique as they are potentially process able and biodegradable and biocompatible polymers. Synthesis of carbohydrate polymers based on sugar, sorbitol, maize starch, acid anhydrides (phthalic and maleic) and small quantity of oxalic acid and citric acid has been attempted. The oxalic acid and citric acid have been specially used to study their effect on foam, detergency and stain removing characteristics. In this synthesis various catalysts like HCl, sodium bisulphate, sodium bisulphite have been used.

The detergents made out of acid slurry cause harm aquatic flora and fauna. Acid slurry has a petroleum origin. The detergents are responsible for foaming and eutrophication. By using vegetable based polymers in detergent formulations the above mentioned problems of water pollution can minimized to greater extent.

Material and Methods

Preparation of Novel Polymers: The synthesis of polymers was carried out in a glass reactor. The reactor consists of two parts. Lower part of the reactor is a round bottom vessel with very wide mouth. The upper part of the reactor is its lid, having four necks with standard joints. 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. And the further neck was used for dropping the chemicals in to the reactor. The reactor was heated by an electric heating mantle having special arrangement for smooth control of the temperature of the reactor. A regulator controlled the speed of the stirrer. The reaction vessel and its lid were tied together with help of clamps. In our earlier experiments we have successfully prepared polymeric surfactants based on natural products of vegetable origin like maize starch, sorbitol, vegetable oils and glycerin in synthesis of polymeric surfactant along with acid anhydride like maleic and phthalic anhydride. These novel polymers have been successfully used in formulation liquid, powder and cake detergents as partial or total replacement of acid slurry of petroleum origin.

Now in the present work we wish to incorporate sugar which is abundantly available throughout the world and small quantity of oxalic acid and citric acid which can step up the polymeric surfactants in reference to foaming, detergency and reduction of surface tention. Sugar on hydrolysis with water splits to glucose and fructose which are potential source of hydroxyl groups for additions of ingredients refer

Neutralization of Polymers: The sample of polymer is taken in beaker and neutralized with 30% KOH solution are maintained at 60^0 C. with constant stirring till ph of 8.0 was achieved.

Analysis of Polymers: Physicochemical analysis and Spectroscopic analysis for prepared polymers were undertaken. For physicochemical properties the standard techniques have been used to evaluate various conventional constants.

Preparation of Powder Detergent: The various ingredients and the composition of detergents powder are as shown in the formulations. The said ingredients in the powdered form are weighed and mixed thoroughly in a tray. Then add liquid ingredients like linear alkyl benzene sulphonate, Alpha olefin sulphonate and neutralized resin. Whole mass is then homogenized thoroughly. This mixture then added in a homogenizer pot. After mixing, the homogeneous mass thus obtained is taken out in a try and kept out in open air for drying.

Preparation: A special type of Whitener is developed by addition of Titanium Dioxide (50%) and Sorbitol (50%) both these are taken in mortar and pestle, triturated for about 1 hrs. and then 1% of this mixture is added to the composition. Robin Blue paste is prepared by mixing robin blue and sorbitol in 1:1 praportion. This paste in added to the composition of powder detergents

Results and Discussion

Powder Detergents: In the synthesis of novel carbohydrate polymers ingredients products like sugar, starch and sorbitol have been used. Maize starch has been used in powder form while sorbitol and sugar can been used in liquid form. These compounds will provide OH groups for esterification and other reactions. Small quantity of citric acid and oxalic acid has been used. There presence in the polymers give better detergency to novel polymers. These compositions have come up after doing several polymers to develop a product with good viscosity, molecular weight and foaming property. These three are selected trials which give excellent performance properties a combination of HCl, sodium bisulphate, sodium bisulphite has been used in all formulation.

The exact cooking schedule of three polymers is given in Table 2.The % yield in all the batches is of order of 90 to 94%. In various batches maleic anhydride has been used the possible chemical reaction are esterification of OH group in carbohydrate ingredients and acidic groups in maleic and phthalic anhydride. A small quantity of benzoic acid has been used as chain stopper citric acid and oxalic acid have been incorporated with a view of improving detergency.

Conclusion

Sorbitol, sugar and starch based surfactants can be used successfully for formulations of powder detergents. A combination of small amount of organic acids like oxalic acid, phthalic anhydride and citric acid in polymer give excellent properties for detergent formulations. Particularly use of oxalic and citric acid helps in improving detergency. Conventional activities can be replaced by these novel polymers to the extent of 50 to 90% without affecting detergency. The foam is normally adversely affected in many compositions.

Sugar and starch can be used in combination with sorbitol, without affecting adversely the property of detergents. We can reduce the amount of petroleum based actives to the extent of 50-80% this is very important achievement. As we are formulating a product which is vegetable based.

The use of 1% HCl as catalyst is giving positive results. The use of sodium bisulphate (1.5%) and sodium bisulphate (0.5%) give good color and homogeneity to product. The following samples have been identifies as excellent. PD1, PD3, PD4 and LD2, LD3. In formulation B1 a small quantity of benzoic acid which helps in regularization.

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References

1. Paolo zini, Polymeric Additives for high performing detergent, Technomic publication, U.S.A**. (1995)**
2. Bauvy A. and Leversidge P., Polymeric surfactants and their use industrial application paint India, 45-52 **(1985)**
3. Polymeric surfactants *Surfactant Science Series,* **(42) Marcel Dekker New York,** Marcel Dekker, Inc, New York, (1992), 165-176**,** 203-205 **(2003)**
4. http://www.Elesvier, “Carbohydrate polymer”.
5. Goddard, E.D., JOACS, **71(1),** 1-15 **(1994)**
6. Gogte B.B., Agarawal R.S., J. Soaps, *Det. Toilet Rev.,* 19-2234 **(2003)**
7. Gogte B.B. and Sorbitol based polymeric surfactant for detergent powder, soaps detergents and toiletries, 25-28 **(2003)**
8. Gogte B.B., Patil P.V., *J. Chem. Engg. World,* **(40),** 71-75 **(2005)**
9. Gogte B.B., Dontulwar J.R., *Asia. J. Chem.,* **16(3),** 1385-1390 **(2004)**
10. Kharkate S.K,.Karadbhajne V.Y., Gogte B.B., Journal of scientific and industrial research, **(64),** 752-755 **(2005)**
11. http://www.nfusugar.com
12. ASTM Standard method, (For acid value of organic coating materials), published by the American society for testing materials, Philadelphia, 1639-70 **(1981)**
13. BIS methods for the test for detergency for household detergent, BIS4995 **(2000)**

14. Haries,"Detergency Evolution and Testing ", Wiley-interscience Publisher, 92-103 **(1954)**

15. ASTM standard method for NON –volatile contains of resin solutions **(1981)**

16 ASTM Standard methods, for viscosity by ford cup method, 1200-82 **(1982)**

17 BIS methods for the test for detergency for household detergent, BIS4995 **(2000)**

18 Haries, Detergency Evolution and Testing, Wiley-interscience Publisher, 92-103 **(1954)**

Table-1
Composition of Carbohydrate Polymers

Ingredients	Batch B1	Batch B2	Batch B3
Sorbitol (100%)	40.82	-	21.5
Maleic anhydride	3.92	-	3.6
Phthalic anhydride	1.56	4.1	1.4
Sugar (100%)	15.72	41.2	21.5
Maize Starch	7.85	-	26.9
Benzoic acid	0.82	-	-
Oxalic acid	3.92	4.1	3.6
Citric acid	3.92	-	3.6
glycerol	-	32.9	-
Water	21.41	17.7	17.8
% yield	90.2	92.36	94.08

All data is reported for 100% solids. Actually Sorbitol was used as 70% solids and Sugar was also used as 70% solids. HCl (1%) was used as catalyst in B1, B2 and B3 and Sodium bisulphate (1.5%) and sodium bisulphate (0.5) has been used as catalyst in all batches.

Table-2
Cooking Schedule of Polymers (Temp. in °c measured after cooking period of sec.)

Sr.no.	Initial temp.	Batch B1	Batch B2	Batch B3
1	After o min.	0	0	0
2	After 30 min.	80	80	80
3	After 60 min.	130	110	110
4	After 90 min.	130	130	130
5	After 120 min.	130	130	130
6	After 150 min.	130	130	130
7	After 180 min.	130	130	130

Table-3
Physico- Chemical Analysis of Novel Carbohydrate Polymers

Sr. no.	Test	Batch B1	Batch B 2	BatchB3
1	%solid	91.09	91.45	96.5
2	Acid value	63	32.25	61.47
3	Viscosity(by ford cup no.4at 30c in seconds)	340	312	514
5	Solubility (soluble in)	water	water	Water
6	PH. value	3.92	3.25	4.83
7	Molecular weight	5179.14	4892.6	5186.4
8	Ester value	488	219.55	171.12
9	Epoxy value	14.40	28.02	13.83

Table-4
Stain Removing Characteristics of Various Polymers

Sr. No.	Medium	Batch B1	Batch B2	Batch B3	S.L.S.	S.L.E.S.	Acid slurry
1	Soil	91.90	93.06	92.65	81.66	85.6	85.3
2	Tea	86.48	78.37	85.32	79.25	77.94	79.51
3	Coffee	88.57	80	87.54	85.34	85.26	85.14
4	palak	92.5	80	92.51	91.57	90.87	91.47

Table-5
Powder Detergent Based on These Polymers

Sr. No.	Ingredients	PD1	PD2	PD3	PD4
1	Our Polymer (B1)	10.52	18.86	10.30	14.81
2	Acid Slurry	1.04	-	1.02	2.40
3	A.O.S.	1.04	-	1.02	2.40
4	S.L.S.	5.26	4.71	5.15	4.81
5	Dolomite	31.57	27.30	29.91	27.92
6	Sodium carbonate	30.57	27.30	28.83	27.92
7	S.T.P.P.	4.26	4.71	5.15	4.81
8	Urea	3.15	2.73	3.08	4.81
9	Sodium Sulphate	5.26	4.61	5.10	2.79
10	E.D.T.A.	0.20	0.18	0.20	0.19
11	Whitener	4.00	6.27	7.11	5.04
12	% moisture	2.13	2.41	3.05	2.10
	Total	100	100	100	100

*PD1, PD2, PD3, PD4 –All samples are based on our polymer (B1)

Table-6
Analysis of Powder Detergents-at 1.0% conc.

Sr.No.	Powder detergent	Foam volume in (cm3)foam stability after 0,5,7,10 min.				Density	Surface tension Dynes/cm
1	PD1	900	0.9985	900	850	0.9985	30.93
2	PD2	950	0.9958	950	950	0.9958	36.28
3	PD3	1000	0.9985	950	950	0.9985	33.10
4	PD4	1000	0.9981	950	900	0.9981	35.58
5	CD1	1000	0.9996	1000	950	0.9996	62.11
6	CD2	1000	1.02	1000	950	1.02	62.35

Table-7
Effect of Powder Detergent on %Detergency
Soil Stain on polyester, tericot, and cotton cloth samples

R0-Reflectance measured on clean cotton cloth = 100, Rs- soiled cotton cloth = 33
R0-Reflectance measured on clean polyester cloth = 100, Rs- soiled polyester cloth = 32
R0-Reflectance measured on clean tricot cloth = 100, Rs- soiled tricot cloth = 32

Sr. No.	Powder detergent	Conc.%	Polyster	Tericot	Cotton
			detergency	detergency	detergency
1	PD1	0.1	91.17	83.82	92.53
2		0.25	94.11	86.76	92.53
3		0.5	95.58	92.64	95.52
4		1	97.05	92.64	95.58
1	PD2	0.1	94.11	80.88	92.53
2		0.25	94.11	85.29	95.52
3		0.5	97.05	89.70	95.58
4		1	98.52	94.11	97.05
1	PD3	0.1	86.76	85.29	92.64
2		0.25	91.17	86.76	95.52
3		0.5	94.11	92.64	95.52
4		1	95.58	94.11	95.58
1	PD4	0.1	82.35	80.88	85.29
2		0.25	85.29	83.82	86.76
3		0.5	86.76	85.29	88.23
4		1	88.23	86.76	89.70
1	CD1	0.1	88.23	91.17	86.76
2		0.25	91.17	94.11	89.70
3		0.5	94.11	95.58	92.53
4		1	95.58	97.05	92.64
1	CD2	0.1	91.17	85.29	82.08
2		0.25	92.64	89.70	85.07
3		0.5	95.58	94.11	89.55
4		1	97.05	98.52	92.64

Table-8
Composition of Selected Liquid Detergent

Sr.No.	Ingredients	LD1	LD2	LD3
1	Acid Slurry	7.5	-	-
2	Alpha Olefin Sulphonate	7.5	-	-
3	Sodium laryl Sulphate	7.5	-	7.5
4	Sodium Laryl ether sulphate	10	10	10
5	Sodium Sulphate	5	5	5
6	Urea	3	3	3
7	Sorbitol	10	10	10
8	Water	49.5	49.5	49.5
9	Our Polymer (B1)	-	22.5	15.0
10	**TOTAL**	100	100	100

LD1-based on original composition, LD2, LD3- based on resin B1

Table-9
Analysis of liquid Detergents-at 1.0% conc.

Sr.No.	Liquid detergent	Foam volume in (cm3)foam stability after 0,5, 7,10 min.				density	Surface tension Dynes/cm
1	LD1	950	1000	1000	1000	0.8308	32.59
2	LD2	950	950	950	900	0.8325	32.64
3	LD3	1000	1000	950	950	0.8402	32.69
4	CLD1	1000	950	950	900	0.8356	32.15
5	CLD2	1000	950	950	950	0.8369	32.27

*CLD- Commercial Liquid Detergent available in the Market

Table-10
Effect of Liquid Detergent on %Detergency
Soil Stain on polyester, tricot, and cotton cloth samples

R0-Reflectance measured on clean cotton cloth = 100, Rs- soiled cotton cloth = 33
R0-Reflectance measured on clean polyester cloth = 100, Rs- soiled polyester cloth = 32
R0-Reflectance measured on clean tricot cloth = 100, Rs- soiled tricot cloth = 32

Sr.No.	Liq. detergent	Conc.%	Polyster detergency	Tericot detergency	Cotton detergency
1	LD1	0.1	86.76	83.82	91.04
2		0.25	88.23	85.29	94.02
3		0.5	89.70	86.76	94.11
4		1	91.17	88.23	94.11
1	LD2	0.1	86.76	83.82	91.04
2		0.25	91.17	80.88	91.17
3		0.5	92.64	82.35	94.02
4		1	95.58	91.17	94.11
1	LD3	0.1	85.29	82.35	94.11
2		0.25	89.70	86.76	91.04
3		0.5	91.17	91.17	91.17
4		1	94.11	94.11	94.02
1	CLD1	0.1	85.29	80.88	91.04
2		0.25	89.70	86.76	91.17
3		0.5	94.11	88.23	94.02
4		1	95.58	95.58	94.11
1	CLD2	0.1	85.29	88.23	95.58
2		0.25	88.23	92.64	83.82
3		0.5	91.17	94.11	88.23
4		1	94.11	95.58	94.11