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Synthesis of Green Liquid Detergents using Carbohydrate Polymers Based on White Dextrin, Sorbitol and Maleic Anhydride

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In present studies, we report the synthesis of carbohydrate polymers based on dextrin, sorbitol and maleic anhydride, with reference to application as detergent. The synthesis of ecofriendly liquid detergent based on carbohydrate origin and the percent composition of the constituents are presented. Physico-chemical properties, the detergency parameters like surface tension reduction of water at various concentration of detergent, foam volume, per cent detergency are also discussed.

Key Words: Carbohydrate polymer, Liquid detergent, Foam volume, Surface tension reduction.

INTRODUCTION

In the present era of petroleum products, the biggest sufferer on the earth is man himself. Uncontrolled application of petroleum based products has caused an extensive damage to the environment occurring to the application of non biodegradable materials which poses great threat to the environment. As we know today, majority of detergents contain the petroleum products only and this dependence of detergent industry on petroleum products needs to be minimized. The detergents are formulated by using linear alkyl benzene sulfonate, α-Olefin sulphate, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium tripolyphosphate, carboxy methyl cellulose, Na_2CO_3, $NaHCO_3$, *etc*. To deal with such kind of situation one needs to discover new raw materials for the synthesis and formulation of detergents. The focus of present work is a successful attempt towards replacement of linear alkyl benzene sulfonate, α-olefin sulphate, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium tripolyphosphate by carbohydrate polymers as basic raw materials. The successful synthesis of carbohydrate polymer using white dextrin, sorbitol and maleic anhydride was discussed elsewhere[1]. This polymer has shown biodegradability and hydophilic liphophilic balance value indicates its application in the field of detergents.

The various green liquid detergents have shown excellent functional characteristics of detergent performance. The important performance parameters like surface tension reduction and foam volume determined and per cent detergent values are very much comparable to the conventional detergent of petroleum origin. The underlining aspect of liquid detergents is that almost 80 % of ingredients is water alone. Such category of detergents is very easy to use and easily dispensable. Owing to these feature, throughout the globe, the application of liquid detergent is popularized.

In the previous work[1], the synthesis and characterization of biodegradable polymer from white dextrin, sorbitol and maleic anhydride was discussed. The synthesis and applications of detergent based on white dextrin, sorbitol and maleic anhydride was also discussed[2]. The present work encompasses the application of the polymer with reference to its detergent formulation and its performance.

EXPERIMENTAL

The synthesis of polymer was discussed elsewhere[1]. Table-1 describes the composition of the green polymer.

TABLE-1
SYNTHESIS OF POLYMER BASED ON WHITE DEXTRIN, SORBITOL, GLYCEROL, MALEIC ANHYDRIDE (COMPOSITION % BY WEIGHT)

Raw material	Batch
White dextrin	30.76
Sorbitol	53.86
Maleic anhydride	15.38

Preparation of liquid detergent: Various raw materials in liquid detergent like neutralized acid slurry, neutralized polymeric resin and conventional ingredients were taken in a glass reactor and homogenized by stirring for *ca.* 0.5 h. The

TABLE-2
COMPOSITION OF LIQUID DETERGENT USING SODIUM HYDROXIDE NEUTRALIZED POLYMER (% WEIGHT METHOD)

Raw materials	AJ1	AJ2	AJ3	AJ4	AJ5	AJ6
Sodium hydroxide neutralized polymer (100 %)	5	5	3	2	5	5
Sodium hydroxide neutralized acid slurry (100 %)	5	5	7	8	5	5
Sodium lauryl sulfate	1	1	1	1	1	1
Sodium lauryl ether sulfate	1	1	1	1	1	1
Ethylene diamine tetra-acetic acid	10	8	5	2	0	5
Sodium tri-poly phosphate	0	2	5	8	10	0
Sodium sulfate	0	0	0	0	0	5
Carboxy methyl cellulose	1	1	1	1	1	1
Water	77	77	77	77	77	77

solution was cooled in refrigerator at 10 °C for 48 h. The clear liquid solution was filtered and packed in superior grade air tight plastic containers. The various formulations of detergent are presented in Table-2. The density and viscosity of the detergents are summarized in Table-3

TABLE-3
PHYSICO-CHEMICAL PROPERTIES OF LIQUID DETERGENT

Sample	Density (g/mL)	pH Value	Viscosity time (s)
AJ1	0.972	8	70
AJ2	0.971	8	60
AJ3	0.970	8	75
AJ4	0.972	8	68
AJ5	0.974	8	65
AJ6	0.973	8	40

Surface tension values were determined using stalagmometer method[3]. The results are presented in Table-4.

TABLE-4
STUDY OF SURFACE TENSION OF WATER AT VARIOUS CONCENTRATIONS OF DETERGENTS

Sample	Concentration (%)	Surface tension (dyne/cm)	% Reduction in surface tension of water
AJ1	0.10	50.26	29.39
	0.25	40.41	43.22
AJ2	0.10	55.45	22.09
	0.25	49.82	30.82
AJ3	0.10	55.90	21.46
	0.25	52.89	25.69
AJ4	0.10	55.96	21.38
	0.25	51.27	27.97
AJ5	0.10	43.96	38.24
	0.25	38.20	46.27
AJ6	0.10	40.38	43.27
	0.25	37.33	47.55
Surf excel liquid	0.10	16.28	77.13
	0.25	15.95	77.59

Determination of foam volume[4]: Foam is coarse at dispersion of gas in relatively small amount of liquid or it may be defined as collection of bubble. Bubbles vary in size from 50 μm to several mm. The low foaming tendency of surfactant is an important property in some recent application. The relationship of foaming power to detergency has always been of interest and foaming power has become associated in many consumers' mind with high deterging power. However, foam has no direct relationship with detergency in ordinary fabric washing system and does not improve cleaning in a laundry or home washing machine. Indeed excessive foam can inhibit agitation and reduce cleaning. Additionally excess foam levels may concentrate certain surfactant in the foam reducing their contact with the fabric to be washed. Foam prevents re-deposition and enables the soil to be easily removed by scrapping off or rinsing away the soil-laden foam.

The volume of foam produced is very important property of surface active materials. Ability to foam at extreme dilution or under adverse condition may be an important factor in application. Bubble Cylinder Method was used to determine the foam characteristics in terms of volume in the present work. To 1000 mL cylinder provided with stopper 100 mL solution of particular concentration was taken whose foam characteristics was to be determined. 30 up-down rotation within time period of 30 s were given to it. The cylinder was kept on table and observed the foam above liquid level and reading was noted down at the interval of 5 min. Same procedure was carried out for the solution with other concentration like 0.1, 0.25, 0.5 and 1.0 %. The results are presented in Tables 5 and 6.

TABLE-5
STUDY OF FOAM VOLUME AT 0.1 % CONCENTRATION OF DETERGENT

Sample	Foam volume (cm^3) in time (min)				
	0	5	10	15	20
AJ1	50	50	40	40	40
AJ2	0	0	0	0	0
AJ3	40	40	40	40	40
AJ4	0	0	0	0	0
AJ5	20	20	20	10	10
AJ6	40	40	40	30	30
Surf excel liquid	121	119	111	111	111

TABLE-6
STUDY OF FOAM VOLUME AT 0.25 % CONCENTRATION OF DETERGENT

Sample	Foam volume (cm^3) in time (min)				
	0	5	10	15	20
AJ1	70	60	60	60	60
AJ2	40	40	40	40	40
AJ3	60	60	60	50	50
AJ4	30	30	20	20	20
AJ5	30	30	30	30	30
AJ6	50	50	40	40	40
Surf excel liquid	142	133	131	118	118

Per cent detergency[5,6]: Per cent detergency was determined in soil, coffee and tea mediums as follows:

Soil medium: The soil medium was prepared by mixing carbon (28.4 %), coconut oil (35.8 %), lauric acid (17.9 %) and mineral oil (17.9 %).

Preparation of soil solution: This was prepared by adding 2 g of above soil paste in 500 mL of carbon tetrachloride solution. Mix it well and use for further cloth sample preparation. The solution is filled up into packed bottle.

Method of application: The cotton cloth of size 24 cm × 32 cm were prepared. Take 50 mL of soil solution in beaker. Dip this cloth sample in it for 5 min. The same cloth dried in open atmosphere for 2 h. Then this cloth was cut into test sample size of 6 cm × 8 cm and these samples were used for washing purpose. The solutions of different concentration as detergent were prepared and heated to 60 °C temperature. Soiled cloth sample was dipped in it for 5 min and given to and for 10 hand washes. Washing was carried out in distilled water only. After rinsing these samples in fresh water are kept for drying purpose. The samples which were washed, dried and ironed were used to find out per cent detergency. The % detergency was determined using lamberts and sanders formula:

$$\% \text{ Detergency} = (Rw - Rs) \times \frac{100}{(Ro - Rs)}$$

where Rw, Rs and Ro are reflectances measured on washed cloth, soiled cloth and clean cloth, respectively.

The reflectance of the cloth samples were measured by using reflectance meter manufactured by Universal Engg. Corporation, Ambala Road, Saharanpur. This was standardized by using the magnesium oxide or tile which was provided along with the instrument. This tile having brightness of 81.3 % was adjusted using the knob provided on instrument. After adjustment was done the samples were kept on the instrument and the readings were noted down and the percent detergency was calculated (Table-7).

TABLE-7
PER CENT DETERGENCY AT VARIOUS CONCENTRATION OF DETERGENT ON SOILED STAINED COTTON CLOTH

Samples	Concentration	Detergency (%)
AJ1	0.10	68.50
	0.25	74.75
AJ2	0.10	62.75
	0.25	67.00
AJ3	0.10	71.50
	0.25	78.00
AJ4	0.10	67.75
	0.25	76.50
AJ5	0.10	66.75
	0.25	72.00
AJ6	0.10	79.50
	0.25	86.75
Surf excel liquid	0.10	75.32
	0.25	78.62

Method of application (tea and coffee): The cotton cloth of size 24 cm × 32 cm were taken and checks were made with the help of size 6 cm × 8 cm. Then the above staining (tea and coffee) solution was taken in a pipette and one drop was added in a center or checks and kept the stained cloth sample in oven at 100-105 °C for 0.5 h. Then this stained cloth was cut into test sample size and these samples were used for washing purpose. The % detergency was determined using lamberts and sanders formula as mentioned above. The results are presented in Table-8.

TABLE-8
PER CENT DETERGENCY AT VARIOUS CONCENTRATION OF DETERGENT ON TEA AND COFFEE STAINED COTTON CLOTH

Sample	Concentration	Detergency (%)	
		Tea	Coffee
AJ1	0.25	65.75	84.61
	0.50	75.75	94.23
AJ2	0.25	81.25	82.63
	0.50	81.75	89.14
AJ3	0.25	72.00	78.10
	0.50	77.75	85.46
AJ4	0.25	60.50	69.05
	0.50	65.50	78.67
AJ5	0.25	71.88	74.71
	0.50	78.10	80.93
AJ6	0.25	74.99	77.25
	0.50	75.84	97.06
Surf excel liquid	0.25	76.30	72.24
	0.50	77.25	75.10

RESULTS AND DISCUSSION

The value of biodegradation ratio, BOD/COD ratio, was found to be 1.12 which extremely favoured biodegradable nature of the polymer and hydrophilic liphophilic balance value was found to be 11.89 which clearly approved the use of polymer for the application as a detergent component[1,2]. The various performance characteristics of detergents like reduction in surface tension, foam volume measurement and percent detergency characteristics have shown that these liquid detergents are good to excellent in few cases. Table-4 of surface tension experiments shows that the sample AJ6 has shown 43.27 % reduction in surface tension at 0.1 % concentration of detergent. In AJ6 50 % polymeric component and 50 % neutralized acid slurry was used and the potent polluting agent STPP was reduced to 0 %. In all other formulations from AJ2 to AJ5 STPP % has been varied from 2 to 10 %. After the observation of surface tension reduction (Table-4), it was observed that the combination of acid slurry and polymeric components bring excellent synergy and helps to show excellent results.

The second cosmetically important parameter to study the functional characteristics of detergents was foam volume. In todays context this particular parameter appeal to the customer. It is evident from Tables 5 and 6 at 0.10 and 0.25 % concentration of detergents respectively, the foam volume of AJ1 to AJ6 series was found to be 50 % to that of conventional liquid detergents in spite of bare minimum application of foam inducing agents.

All samples from AJ1 to AJ6 have shown excellent % detergency value than conventional sample of surf excel liquid in case of coffee stained cotton cloths. The samples AJ2 to AJ5 have shown equivalent performance of cleaning a tea stained cotton cloth.

Conclusion

Green liquid detergent formulations are seemingly promising replacement for petroleum products. Green liquid detergent popularization would be acceptable to the masses as it would be cheaper than powder detergents. Green liquid carbohydrate polymer detergent will be pollution free and economically viable alternative Green liquid detergent formulation would be sustainable replacement for non renewable petroleum product.

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