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LIQUID GLUCOSE BASED POLYMERS AS ACTIVE INGREDIENTS IN LIQUID AND POWDER DETERGENTS

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ABSTRACT

Various Natural Grains, Cereals, Legumes, Fruits and Honey contain 38-75% of glucose which can be used in the synthesis of polymeric surfactants. In the present work liquid glucose and sorbitol obtained from corn by using steeping and enzymatic liquefaction process have been used for synthesis of polymer. The time of reaction, temperature and mole ratio have been standardized and physicochemical and spectroscopic analysis of polymers has been carried out. H.L.B. value and other characteristics suggest the use of these polymers in powder and liquid detergents compositions. Typical liquid and powder detergents have been formulated and compared with commercial products. Inclusion of 8-10% of polymers gives satisfactory performance characteristics. These polymer and detergent compositions should be tried on industrial scale.

Key Words: Liquid Glucose, Sorbitol, Powder and Liquid Laundry Detergents

INTRODUCTION

Liquid glucose[1-3] obtained from steeping and enzyme reaction on corn starch[4-5] is valuable material used in sweets, bakeries and confectionary products. Table no. 1 gives the %

available glucose in various grains, legumes, fruits and honey. There is steep increase in production and utilization of corn products in India, Canada, U.S.A. and other countries. All the household cleaning preparations like sanitizers, utensil cleaners, glass cleaners and cloth washing products like powder, cake and liquid detergents[6-8] are based mainly on Linear Alkyl Benzene Sulphonate and Alfa Olefin Sulphonate of petroleum origin. We must think of replacing these crude petroleum based products with corn products like liquid glucose and sorbitol. In the present research efforts Novel polymers have been synthesized based mainly on liquid glucose and sorbitol. Smaller amounts of maleic anhydride, citric acid and oxalic acid have been used in synthesis of polymers. Sodium bisulphate ($NaHSO_4$) and sodium bisulphate ($NaHSO_3$) have also been used in small proportions. They will catalyze the process of esterification and can react with –OH group in the polymer to form SO_3Na groups in the polymer. The idea is to get an active material which can wholly or partly replace Acid Slurry or AOS of petroleum origin.

Selected polymers have been used in preparation of powder and liquid detergents as partial or total replacement of Acid Slurry and Alpha Olefin Sulphonate.

Table No. 1

% of Glucose in available natural products

Sr. No.	**Natural Products**	**% Glucose**
1	High Fructose Corn Syrup	75
2	Cereals	50
3	Legumes	7.4
4	Fruits	62-79
5	Honey	38

Table No. 2

Composition of Novel polymers Based on Liquid Glucose and Sorbitol

Sr. No.	Name of Batch → % Ingredients ↓	B4	B5	B7	B8
1	Liquid Glucose	40	40	40	50
2	Sorbitol	43	43	43	33
3	Citric Acid	10	-	-	-
4	Oxalic Acid	-	10	-	-
5	Maleic Anhydride	-	-	10	10
6	Sodium Bisulphate	3.5	3.5	3.5	3.5
7	Sodium Bisulphite	3.5	3.5	3.5	3.5

Experimental

The polymers prepared were analyzed with respect to the parameters mentioned in Table No. 3.

Table No. 3

Physico Chemical Analysis of Polymer based on Liquid Glucose and Sorbitol

Sr. No.	Parameters Analyzed	B4	B5	B7	B8
1	Acid Value	112.6	98.4	49.0	52.3
2	SAP Value	45.9	95.2	42.4	104.1
3	HLB Ratio	18.6	17.7	18.8	17.2
4	Density 1% solution (gm/cm)	1.04	1.01	1.01	1.01
5	Foam (1% solution) in CC By Cylindrical Method	100	120	100	100
6	pH of 1% solution (pH meter)	4.18	3.89	3.20	3.16

7	Solubility in water	Soluble	Soluble	Soluble	Soluble
8	Viscosity by Fort cup No.4 at 30^0C (second)	175	170	285	215
9	Color and Transparency	Brown and Transparent	Brown and Transparent	Honey color and transparent	Honey color and transparent
10	% Solids	73.52	78.9	78.4	77.06

Some compositions of powder and liquid laundry detergents based on polymer sample were preparedas shown in Table No. 4 and 6. These samples were analyzed for different physiochemical characteristics are compared with commercial samples as shown in Table No. 5 and 7.

TableNo.4

Composition of Powder Detergents Based on Liquid Glucose Containing Polymer

Ingredients → Samples ↓	**Polymer B4 B8**	**LABS**	**AOS**	**SLES 40%**	**SLS**	**Sorbitol 70%**	**CMC**	**Sodium Carbonate**	**SS**	**Salt**	**TiO_2 Paste**
PDB4 1	5	5	3	1	1	1	1	35	14	30	4
PDB4 2	6	4	3	1	1	1	1	35	14	30	4
PDB4 3	7.5	2.5	3	1	1	1	1	35	14	30	4
PDB4 4	10	0	3	1	1	1	1	35	14	30	4
PDB8 1	5	5	3	1	1	1	1	35	14	30	4

PDB8 2	6	4	3	1	1	1	1	35	14	30	4
PDB8 3	7.5	2.5	3	1	1	1	1	35	14	30	4
PDB8 4	10	0	3	1	1	1	1	35	14	30	4

LABS = Linear Alkyl Benzene Sulphonate, SLS =Sodium Lauryl Sulphate, AOS = Alpha Olefin Sulphonate, SLES = Sodium Lauryl Ether Sulphate, CMC =Carboxyl Methyl Cellulose, SS = Sodium Sulphate, TiO_2 Paste = 30% TiO_2 powder in 70% polymer.

Table No. 5

Performance characteristics and Detergency Evaluation of Powder Detergents Based on Liquid Glucose

Sample	**Foam (Cylindrical method)in CC**		**Density gm/lit**	**Surface tension (Dyne/cm) Stalagnometer Method**	**% Moisture %**	**pH (1% sol^n)**	**Soil Stain Removal (Std. Method) %**
	0.5%	**1%**					
PDB4 (1)	700	900	1.0104	33.98	3.7	9.6	96.68
PDB4 (2)	700	900	1.0268	33.69	3.6	9.7	94.89
PDB4 (3)	800	1000	1.0056	30.74	3.7	9.82	97.87
PDB4 (4)	650	1000	1.0752	31.67	3.96	9.78	93.61
PDB8 (1)	800	1000	1.0100	37.55	4.5	9.67	95.54
PDB8 (2)	800	1000	1.0100	41.79	4.7	9.65	97.43
PDB8 (3)	700	1000	1.0096	39.56	4.7	9.72	94.59

PDB8 (4)	600	800	1.0048	33.22	5.0	9.73	89.78
Commercial Sample	900	1000	1.0072	19.02	2.08	10.23	98.32

Table No. 6

Composition of Liquid Laundry Detergents Based on Liquid Glucose Composition by Weight

Sample	**Novel Liquid Glucose Based Polymer**		**Alpha Olefin Sulphonate**	**Sodium Lauryl Ether Sulphonate**	**Sorbitol (70% solids)**	**Urea**	**Sodium Chloride**	**Water**
	B4	**B8**						
LDB4 1	10	-	5	20	20	03	03	39
LDB4 2	10	-	4	20	20	03	03	40
LDB4 3	10	-	3	20	20	03	03	41
LDB4 4	10	-	2	20	20	03	03	42
LDB4 5	10	-	1	20	20	03	03	43
LDB8 1	-	10	5	20	20	03	03	39
LDB8 2	-	10	4	20	20	03	03	40
LDB8 3	-	10	3	20	20	03	03	41
LDB8 4	-	10	2	20	20	03	03	42
LDB8 5	-	10	1	20	20	03	03	43

Table No. 7

Performance Characteristics and Detergent Evaluation of Liquid Detergents Cleaning Efficiency

Sample	**Foam in CC (by cylindrical method)** **0.5%**	**1%**	**Density (gm/lit)**	**Surface Tension (Stalagnometer Test) (dyne/cm)**	**% Solids %**	**Cleaning on Soil Stain Cloth 1%**
LDB4 (1)	950	1000	0.9982	30.69	42.2	95.32
LDB4 (2)	950	1000	1.0096	25.73	38.1	95.37
LDB4 (3)	850	950	1.0096	33.19	38.6	90.47
LDB4 (4)	850	930	1.006	33.66	39.6	89.03
LDB4(5)	750	850	1.0104	29.58	33.3	88.56
LDB8 (1)	800	1000	1.0072	34.63	32.9	94.65
LDB8 (2)	950	1000	1.008	36.38	37.7	94.96
LDB8 (3)	900	1000	1.0024	34.46	34.4	93.57
LDB8 (4)	850	1000	1.0024	31.56	34.8	92.38
LDB8 (5)	720	850	1.0100	38.62	32.29	85.69
Commercial Liquid	220	300	0.9948	34.71	15.09	96

Detergent						

Ex= 95-100% stain removal, G= 70-80% stain removal, P= Less than 50% stain removal, VP= Stain not removed

Table No. 8

Evaluation of Cleaning Ability of Samples on Tea, Coffee and Spinach Stained Cloths

Samples	Cleaning of Tea	Cleaning of Coffee	Cleaning of Spinach
PDB4 1	4	4	4
PDB4 2	4	3	4
PDB4 3	3	3	3
PDB4 4	3	3	3
PDB8 1	4	4	4
PDB8 2	3	4	3
PDB8 3	3	4	3
PDB8 4	3	3	3
Commercial Powder Sample	4	4	4
LDB4 1	4	4	4
LDB4 2	4	4	4
LDB4 3	3	4	3
LDB4 4	3	4	3
LDB4 5	3	3	3
LDB8 1	4	4	4
LDB8 2	4	4	4
LDB8 3	4	4	3
LDB8 4	3	4	3
LDB8 5	3	3	3

Commercial Liquid Sample			

Cleaning Points 1- 0 to 25% Cleaning, 2- 26 to 50 % Cleaning, 3- 51 to 75% Cleaning, 4 -76 to 100% Cleaning.

Table No. 9

IR Spectrum of Batch B4

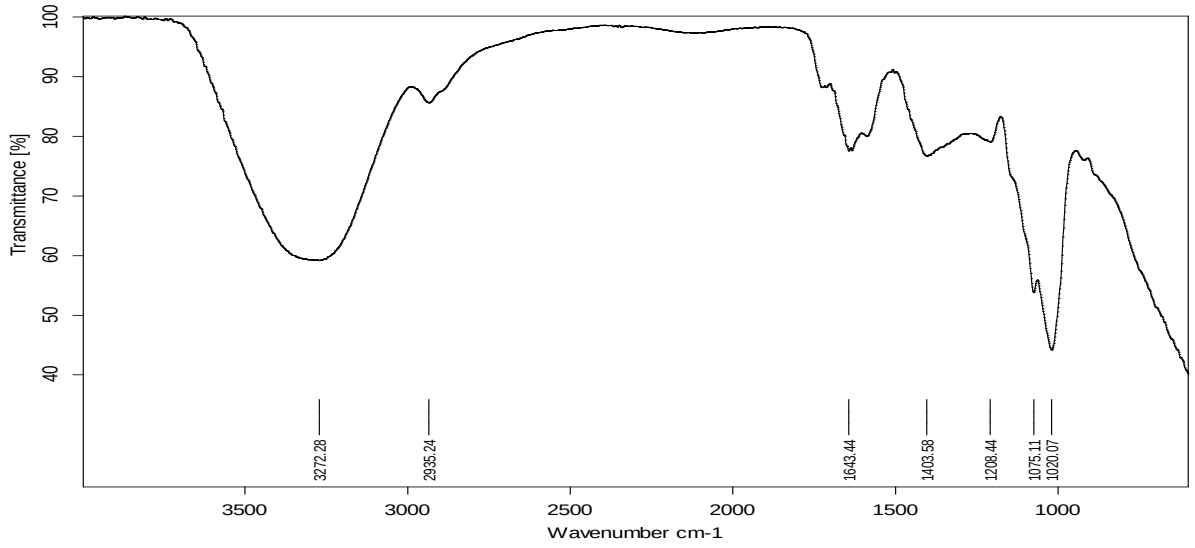

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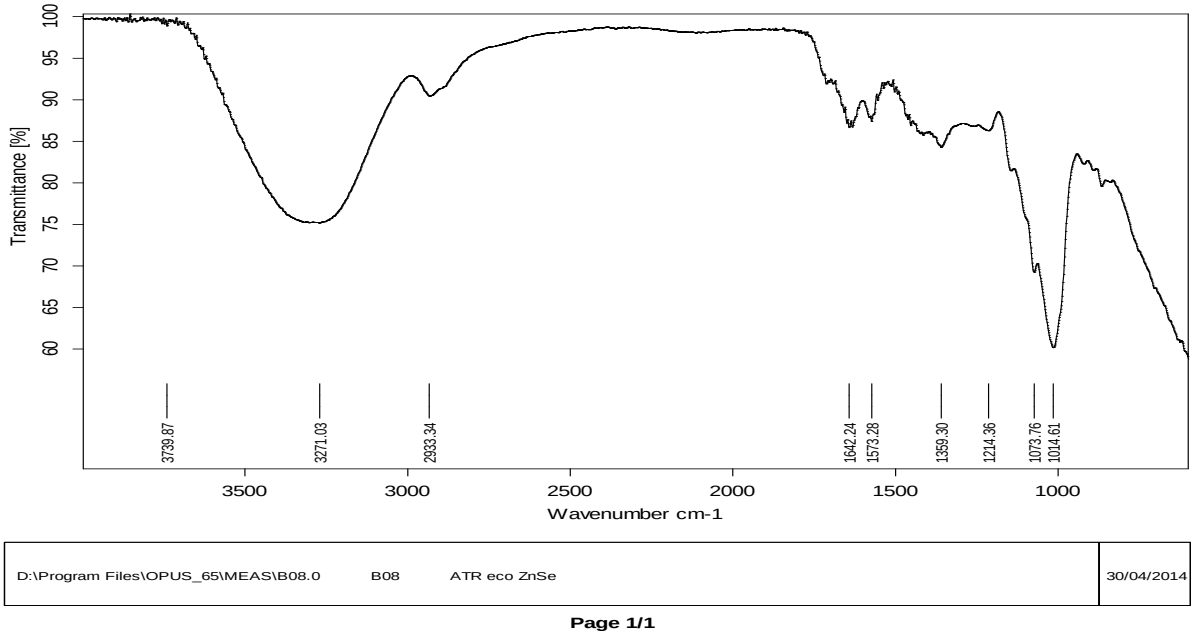
Table No. 10

IR Spectrum of Batch B08



Result and discussion

Table No. 1 give an idea about carbohydrates[9-11] (in the form of sugar or liquid glucose) present in various natural vegetable products. These carbohydrates are used mainly for making sweets, biscuits, cakes and tonics. In fact these materials are available in huge tonnage in many countries. A part of this reservoir can be used for making polymers with acids and use these polymers as replacement of Acid Slurry and Alpha Olefin Sulphonate. In the present Research project we have synthesis polymers based on Liquid Glucose and Sorbitol. These carbohydrates have been reacted with Maleic anhydride, citric acid and oxalic acid to get useful polymeric surfactants[12-14]. A small quantity of sodium bisulphate and sodium metabisulphite has also been used which will catalyze esterification and also react with –OH groups to give useful surfactants properties to the polymer.

The physiochemical analysis of polymer is given in Table No. 2. The acid value of polymers shows the presence of free acid groups in the polymer. These acids groups can be neutralized to get highly water soluble polymers. The HLB ratio[15] indicates the utility of these polymers in powder and liquid detergents. The products as such do not show any foaming property. The samples have acidic pH of 3 to 4. The viscosity of sample is suitable for handling and use in detergent compositions. Compositions have a % solid of 76-78%. All samples have high water solubility.

The compositions of powder detergents based on polymer B4 and B8 is shown in Table No. 4. In progressive samples Acid Slurry has been replaced by polymer from 20-100%. The proportions of other conventional ingredients are kept constant in all formulations. Titanium oxide paste containing 30% in TiO_2 powder in these polymersis used as an additive which will give ultimately white and bright appearance to cloths.

Foaming, surface tension and soil stain removal characteristics are recorded in Table No. 5. All samples have excellent foaming property at 0.5 to 1% concentration. These properties are comparable to commercial sample tested simultaneously.

There is excellent surface tension reduction in all samples and it is comparable to commercial sample. Soil stain removal is excellent for all compositions. In Europe and Africa liquid detergents have almost replaced powder and cake detergents. It is the need of hour to replace powder and cake detergent in Asia and Africa with liquid detergents. Liquid detergent useful in tropical climates needs special attention. A reasonably moderate price for this material is essential so that these liquid can be marketed in third world country.

The composition of liquid laundry detergents based on our polymers is shown in Table No. 6. All samples contain 10% of polymer and a small quantity of Alfa Olefin Sulphonate. All other ingredients are common ingredients used traditionally in formulations.

The performance characteristics and detergency evaluation of liquid detergents is given Table No. 7. The foaming properties at 0.5 to 1% concentration are satisfactory and on par or sometimes betterthan commercial samples. There is significant reduction in surface

tension at 1% concentration. This reduction in surface tension will certainly help in better contact with soiled cloths and soil removal. The reduction in surface tension is comparable to commercial products. The soil stain removal experiments showexcellent soil removal at 1% concentration. This is comparable to commercial products. Table No 8 shows the cleaning ability of the powder and liquid detergents prepared from Batch B4 and B8 with Tea, Coffee, and Spinach stained cloths. After comparing this with commercial samples, they found more natural and eco-friendly.

Table No. 9 and 10 gives the information about Infra-Red Spectrums[16-18] of the batches B4 and B8. According to the spectra it shows the presence of OH- group (in B4 at 3271.28 and in B8 at 3271.03), free carboxylic acid group (in B4 at 1643.44 and in B8 at 1642.23), ether group (in B4 at 1208.44 and in B8 at 1214.38).

Conclusion:-

1) Novel polymers can be synthesis based mainly on liquid glucose and sorbitol. Small proportion of Maleic anhydride, Citric acid and Oxalic acid has been used. The mole ratio, time of heating and catalyst has been standardized which will give optimum performance to liquid and powder detergents.

2) The physico chemical and spectral analysis shows the suitability of these polymers for preparation of liquid and powder detergents.

3) The spectral analysis show definite presence of ester, ether, free acids and free hydroxyl groups in the samples.

4) These samples use minimum quantities of petroleum based surfactants therefore green to use.

5) Powder and liquid detergents based on above polymer show satisfactory performance and stain removing properties.

6) The polymer synthesis and powder and liquid detergents must be tried on pilot commercial scale.

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