

**LIQUID LAUNDRY DETERGENTS BASED ON NOVEL POLYMERIC
SURFACTANTS**

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ABSTRACT

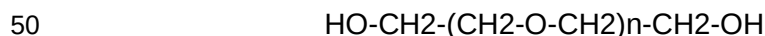
A novel polymer based on sorbitol, polyethylene glycol, citric acid has been synthesized using HCl as catalyst. The experimental conditions, order of addition of ingredients, ratio of ingredients, catalyst, time and temperature have been standardized to get desired molecular weight, HLB ratio and viscosity characteristics. Spectroscopic studies of I.R. & N.M.R. of polymers has been undertaken which reveal presence of ester, ether, free Hydroxyl and free acid groups in the polymer. The selected polymer has been used as replacement of conventional linear alkyl benzene sulphonate in liquid detergent formulations. The compositions are ecofriendly and economical as they depend upon vegetable source polymers.

Keywords: Synthesis, polymer, sorbitol, HLB ratio, viscosity
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36 **1. INTRODUCTION**

37 A large number of industrial products and surfactants are based mainly on
38 various crude petroleum products. For in country we are importing roughly 2/3 rd. of
39 our requirement from other countries. For a healthy and self-sufficient economy and
40 green environment we must think of vegetable alternatives as raw materials for
41 various products. In our laboratory we have successfully used vegetable stocks
42 based polymeric surfactants as replacement of acid slurry to the extent of 50-
43 60%[1]. The products like powder detergents[2] cake detergents[2] and liquid
44 detergents[3], paints[4], wall finishes[5], have already been successfully prepared.
45 These products compete in price and technical performance with present
46 generation commercial products.

47 In the present research work we have planned to synthesize novel polymer
48 based on polyethylene glycol which can replace 80-100% petroleum based acid
49 slurry. Polyethylene glycol (400) is a polymer having structure :



51 It is prepared by polymerization of ethylene oxide. The most important properties of
52 PEG are

53 a) Solubility in water making it ideally suitable for different applications.

54 b) Presence of oxirane oxygen may also help to get a high performance active
55 polymeric surfactant which can replace acid slurry.

56 c) Presence of polyethylene glycol may help in removing stains of ink, soil,
57 Tea, coffee, and spinach [6].

58 The synthesized polymers were analyzed systematically for their acid
59 value[7,8], Saponification value[9] surface tension[10] and other physico-chemical
60 characteristics.

61 **EXPERIMENTAL DETAILS**

62 A glass reactor fitted with stirrer, heating mantle and condenser was set up for the
63 synthesis of the novel polymer. initially, a stoichiometric quantity (Table -1) of
64 sorbitol, polyethylene glycol, citric acid was added in the reactor .concentrated
65 hydrochloric acid was used as a catalyst .The temperature was raised slowly and
66 steadily to 130⁰c for. The reaction was continued for 3 hrs. till the desired viscosity,
67 acid value and molecular weight were achieved. The consistency of the paste was
68 maintained by adding additional water after 0.5 h. at the end of this period the
69 reaction was terminated and the prepared polymer was collected in a glass-
70 stoppered bottle with least air gap. The final yield of the product was weighed. Four
71 different liquid detergent compositions were prepared as detailed in Table-2 these
72 polymers sample were systematically analyzed to know acid value, molecular
73 weight, viscosity, % oxirane oxygen value. the sample was systematically tested for
74 % solids, foam, pH and saponification- value .they were also analyzed by IR and

75 NMR spectroscopy to know the finger prints of ester group, ether group, free-OH
76 groups and free acid groups

77 . The % of polymer and acid slurry were varied from 10 to 16 and 7-1% resp. Table
78 4 and 5 describe the effect of detergent concentration on surface tension, foam
79 height. The testing has been done as per standard methods.(stalagmometer,
80 cylinder method, HBr method, % detergency was also determined by using
81 Reflectance meter.)

82 The acid value (Bacher,1960a), saponification value(Bacher,1960b), oxirane
83 oxygen by HBr method. Formulae are as follows-

84 Acid value= $56.1 \times V \times N / W$

85 V= Volume of alcoholic KOH solution

86 N= Normality of alcoholic KOH solution

87 W= Weight in grams of polymer

88 The acid value of the polymer was determined by dissolving 1 gram of the polymer
89 in 100 ml of neutral ethanol and solution was titrated with 0.1 N KOH solution in
90 presence of phenolphthalein until a pale pink color was formed.

91 Saponification value= $56.1 \times (B-S) \times N / W$

92 B= Blank titration reading

93 S= Sample titration reading

94 N= Normality of alcoholic KOH solution

95 The saponification value of the polymer was determined by refluxing 1 gram of the
96 polymer with 50 ml. of 0.5N HCl in presence of phenolphthalein. A blank experiment
97 was also performed by repeating the entire process without taking the polymer.

98 Oxirane oxygen = $V \times N \times 1.6 / W$

99 V=Volume of HBr solution

100 N= Normality of HBr solution

101 W= Weight of polymer

102 The oxirane oxygen value was determined by dissolving 2 grams of sample in
103 benzene and titrated with 0.1N HBr solution by using crystal violet indicator.

104 Other physical constants were determined . The polymer is believed to be an ester
105 of carbohydrate which was confirmed by spectral studies [11,12,13]. Various peaks
106 and interpretation of peaks indicate presence of ester (1727cm^{-1} , Fig 1 and 2)

107 **Analysis and Testing of Liquid Detergent**

108 Liquid detergents (3 samples) were prepared using different concentrations of
109 polymer with sodium lauryl ether sulphate (SLES), sorbitol, polyvinyl alcohol, sodium
110 carbonate and Acid slurry in a beaker and stirring was continued for 30 min (Table
111 3) The sample was stored overnight at 100°C , in oven. A clear solution of liquid
112 detergent was obtained. The surface tension of liquid detergents was measured
113 using stalagmometer. Foam was measured by using mechanical agitation in a
114 closed glass cylinders of 1 liter capacity. The analysis of different liquid stain removal
115 of sample is given in Table 5 and 6.

116 **Stain Preparation:** The soil medium of following composition was prepared.

117 Component Weight %-carbon black (28.4%), coconut oil(35.8%), lauric acid(17.9%),
118 mineral oil(17.9%). The mixture of carbon black and lauric acid along with mineral oil
119 was taken in a pastel mortar. Coconut oil was added slowly to form a thick paste. All
120 the components were ground in paste for 1-2 hours to obtain fine paste.

121 **Soil Solution:** This was prepared by adding 2gms of above paste in 500ml of
122 carbon tetrachloride. Mix it well and use for staining cloth sample preparation. The
123 solution was kept in packed bottles.

124 **Tea Stain Solution:** The tea was prepared with following composition. Tea (Taj
125 Mahal)(2.2%), sugar(8.0%), milk(38.4%), water(51.4%). 25 gms of water was warmed
126 to 35 to 40°C then add Taj mahal brand tea and sugar heated up to 80°C milk was
127 added then heating continued at boil for next 5 minutes, stop heating and pass the
128 tea through a Steiner. Use this as tea medium.

129 **Preparation of Coffee Medium:** The Coffee of following composition was
130 prepared,

131 coffee (1.0%), sugar (8.1%), milk(51.9%), water(39.0%). 25gms of milk and water in
132 a beaker warmed to 35 - 40°C , coffee and sugar were added and heating continued
133 to the boil for 5 minutes.

134 **Preparation of Palak (Spinach) Medium:** The palak medium was prepared as per
135 following composition, oil (1.34%), palak(9.00%), water(89.66%) heated and fried for
136 5 minutes. To this add half cup of water cooked for 10 minutes after the preparation
137 it was stored in tight bottle.

138 **Method of application of soil:** The cloth of size $24 \times 32 \text{ cm}^2$ were prepared. Took
139 50ml of soil solution in a beaker, the cloth sample was soaked in for 5 minutes. This
140 is kept outside for drying in open atmosphere for 2 hours. Then this cloth was cut in
141 size of $6 \times 8 \text{ cm}^2$ and samples were used for the washing test.

142 **Method of Washing:** The solutions of different concentration were prepared.
143 heated to 60⁰c. soiled cloth sample was dipped in it for 5 minutes and given to and
144 fro 10 hand washes.

145 **Method of application of (Spinach, Tea and Coffee):** The cotton cloths of size 24
146 x 32 cm² were taken and drawn checks of size 6 x 8 cm². Then took the above
147 staining solution in a pipette and added in a center of checks one drop and then
148 kept the stain cloth sample in an oven at 55 – 60⁰c for ½ hr. then this stain cloth was
149 cut into test sample size and these were used for stain removal testing.

150 **Calculation for functional group –**

151 **-OH group**

152 **In Sorbitol-**

153 **Molecular weight of sorbitol- 182**

154 **One mole of sorbitol contains 6 –OH groups**

155 **Number of –OH groups in 75 grams of sorbitol- $6 \times 75 / 182 = 2.47$**

156 **-COOH group-**

157 **In citric acid-**

158 **Molecular weight of citric -192.12**

159 **One mole of citric acid contains 3 _COOH groups**

160 **Number of –COOH groups in 20 grams of citric acid $3 \times 20 / 192.12 = 0.312$**

161 **Determination of % solid-**

162 **Weigh 2 grams of polymer and heat it in oven at 100⁰C for 3 hrs. Cool and weight**
163 **after heating.**

164 **Weight of empty crucible-W1, Weight of crucible+ sample-W2, Weight of crucible +**
165 **sample after heating-W3**

166 **% Moisture- $W2 - W3 / W2 - W1 \times 100$, % solid content= 100-volatile content**

167 **% volatile matter= $[W2 - W3 / W2 - W1 \times 100]$ - % moisture**

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169 **Table-1 Composition of novel polymers based on polyethylene glycol.**

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Serial No.	Raw materials	Concentration (% by weight)		
		VI	A	B
1.	Sorbitol(70% solid)	75	80	60
2.	Polyethylene glycol(400)	05	10	30
3.	Citric acid	20	10	10

171 catalysts = 1% HCl, sodium metabisulphite =3.5%, sodium bisulphate =3.5%

172 isopropanol =2% (as solvent)

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180 **Table- 2**

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182 **Composition of liquid detergents based on combination of Neutralized Acid**
183 **slurry and novel polymer**

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Serial No.	Raw materials	Concentration (% by weight)			
		LA-1	LA-2	LA-3	LA-4
1.	Acid slurry	7	5	3	1
2.	S.L.E.S.	20	20	20	20

3.	Polymer	10	12	14	16
4.	Sorbitol	10	10	10	10
5.	Sodium sulphate	03	03	03	03
6.	Sodium carbonate	7.5	7.0	7.6	7.5
7.	Perfume	0.5	0.5	0.5	0.5
8.	Distilled water	42.0	42.5	41.9	42.0
	Total	100	100	100	100

S.L.E.S- sodium lauryl ether sulphate La- 1,2,3,4 - code for liquid detergents

3. RESULTS AND DISCUSSION

Table 3 PHYSICOCHEMICAL PROPERTIES OF THE SYNTHESIZED POLYMERS

Serial No.	Polymer property	Observations		
		VI	A	B
1.	Acid value of polymer	110	42.01	41.52
2.	pH value of 1% solution	4	3	3

3.	Saponification value	49.56	70.1	51.80
4.	% Solids	81.20	85.65	76.28
5.	Solubility in Water	Soluble	Soluble	Soluble
	Solubility in Xylene	Insoluble	Insoluble	Insoluble
6.	hydrophilic- lipophilic balance	15.19	11.32	11.43
7.	Flow time Ford cup No.4 in second at 30 ⁰ C	258	258	258
8	Surface Tension (in dyne/cm)By stalagmometer	27.5	24.20	19.07
9	% Oxirane oxygen(by HBr method)	3.77	2.9	3.71
10.	*Foam Volume(in cc)By cylinder method	900	950	800

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Table-4 Analysis of liquid detergents at 1% concentration by weight

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Note: Surface tension of Distilled water=72.79 Dyne/cm

Detergent sample	Density(by density bottle)in g/cm ³	Surface tension(by stalagmometer)in dynes/cm	Foam height(by cylinder method)in cc	Flow time(by Ostwald's viscometer) in second
LA-1	0.9556	26.59	1000	180
LA-2	1.019	30.64	750	185
LA-3	1.003	26.59	1000	175
LA-4	1.019	34.01	800	165
Commercial	0.910	37.5	800	200

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The pH of all samples was 8.5-9 at 1% concentration in distilled water

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211

Table-5

Stain removal

Liquid detergents	Soil	Tea	Coffee	Spinach
LA-1	G	Ex	G	Ex
LA-2	G	Ex	G	G
LA-3	G	G	G	G
LA-4	P	P	G	P
Commercial	G	Ex	Ex	Ex

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Abbreviation:

Ex (excellent) :90%, stain removed, G (good): 75%, stained removed, P(poor): 50%, stain removed.

216 Physicochemical properties of the Novel polymer are shown in Table-3. Table
217 -4,5. showed the analysis of the formulated liquid detergents(LA-1, LA-2,LA-3,LA-4)
218 polymeric surfactants give excellent characteristics of foaming, surface tension and
219 cleaning stains of soil,tea,coffee and spinach. Figure(1)and Figure(2) show the
220 N.M.R and IR spectra of polymer VI. Various peaks and interpretation of The peaks
221 indicated presence of ester(1727cm^{-1}), free OH(3380cm^{-1}),-COOH(1423cm^{-1}). in the
222 synthesized polymer. The peak at 1727cm^{-1} is further verified by NMR spectra
223 showing peak 3.70ppm. Free OH at 3380cm^{-1} also verified by NMR by the peaks
224 between 3 and 4 ppm. The peak 3.36 ppm which is an indication that not all the –
225 OH groups of PEG and sorbitol are reacted. The various between the region 3.65 to
226 3.75 indicated the esteric proton in the polymer

227 Three Novel polymers have been synthesized which incorporate 10-30%
228 polyethylene glycol. The samples also use 10-30% citric acid in different
229 compositions. Citric acid is particularly used as it is known for its cleaning and
230 preservative properties. If we look at the structure of citric acid it has three carboxyl
231 groups and one OH group. This particular structure may help in developing polymer
232 having surfactant characteristics. The catalysts used are 1% HCl and 3.5% each of
233 sodium metabisulphite and sodium bisulphate. The yield of polymer is around 90-
234 95% on weight basis. When we use 20% citric acid we get a polymer of higher acid
235 value. All samples show acidic pH. The hydrophilic-lipophilic balance is very
236 important parameter the values of hydrophilic-lipophilic balance the polymers were
237 used in detergent. Hydrophilic-Lipophilic balance value is based mainly on
238 saponification value and acid value of original substance. The hydrophilic-lipophilic
239 balance of the resin is 15.19 which indicated that they can be use as active material
240 for detergent. For detergent formulation HLB (hydrophilic-lipophilic balance) value
241 is calculated by using formula
242
$$\text{HLB} = 20 \left\{ 1 - \frac{\text{Sap. Value of the polymer}}{\text{Acid value of the raw materials}} \right\}$$
 The HLB
243 value of our polymer is 15.19 indicating its use in detergent formulation. (HLB
244 value of polymer for application in detergents is 13-15), indicating the use of
245 polymer as active ingredient in liquid laundry detergents. Desired viscosity of
246 polymer is about 300 and molecular weight is 4000.

247 Several liquid Laundry detergents have been formulated. An effort has been made
248 to replace acid slurry with maximum proportion of polymer. The proportion of
249 S.L.E.S.(38%) and sorbitol 10% has been maintained constant.

250 The physico- chemical and performance characteristics of Liquid detergents are
251 shown in Table-4

252 The samples were also compared with commercial laundry detergents available in
253 the market. Our samples are at par or sometimes better than the commercial
254 products in reference to foaming, surface tension and cleaning of the stains of soil,
255 tea, coffee and spinach.

256 The costing of samples is quite satisfactory and these products can be taken on
257 pilot plant and commercial scale.

258 Two possible chemical reactions occurred as follows:

- 259 1) Esterification reaction between acid group of citric acid and –OH group of
260 sorbitol and polyethylene glycol.
- 261 2) Etherification reaction between two- OH groups of polyethylene glycol and
262 sorbitol to produce ethoxy groups.
- 263 3) Both these reaction are expected to give good surfactant property.

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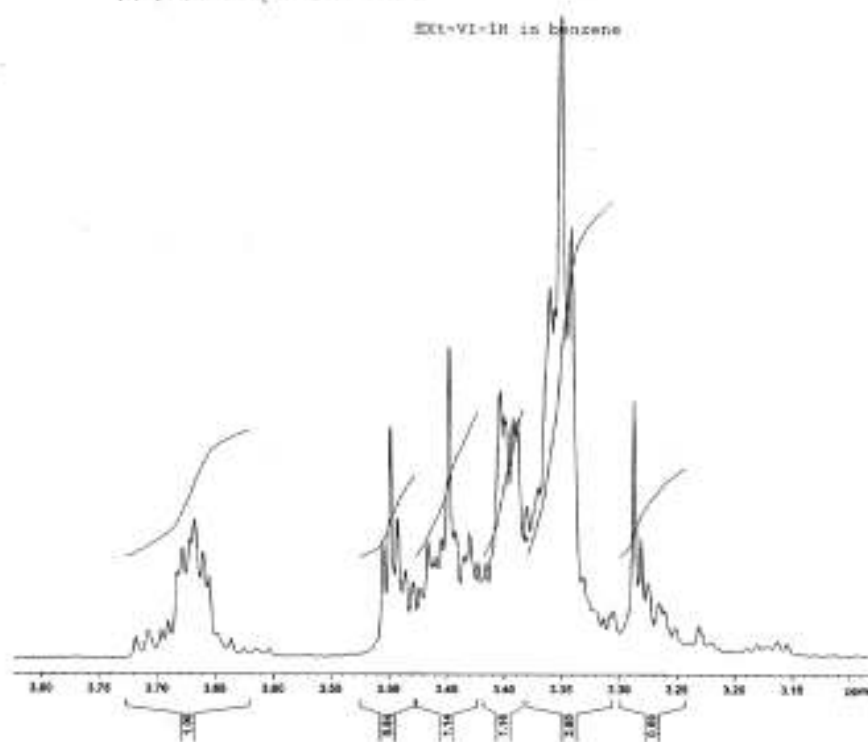
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280 Fig. 1 and Fig. 2

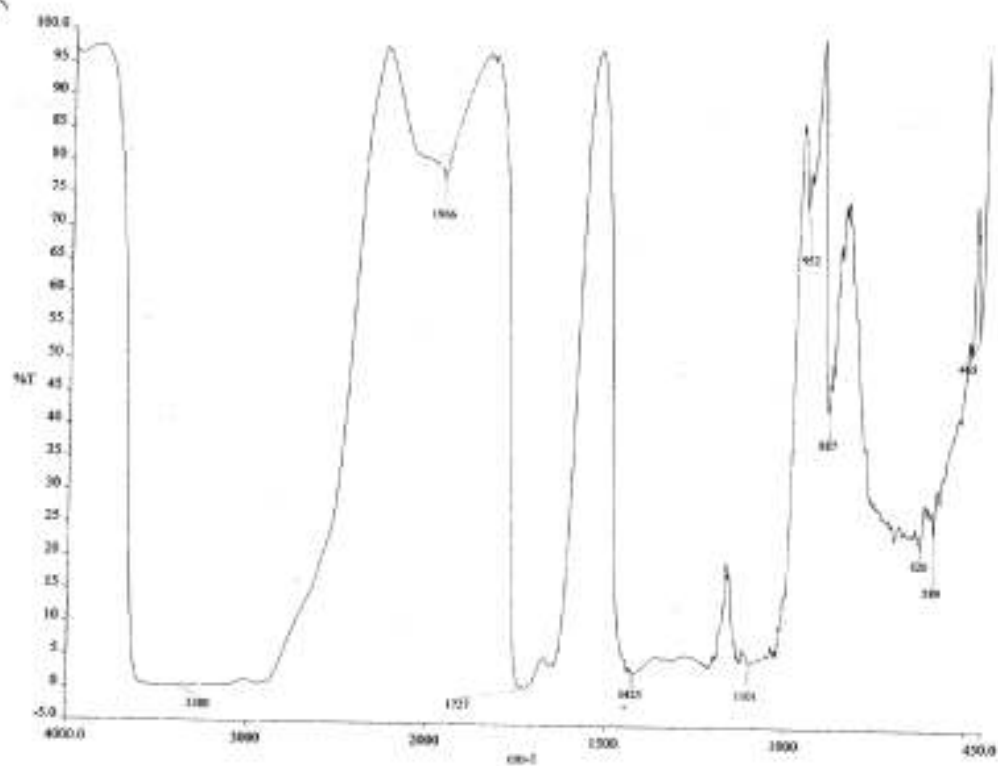
281 *NMR and IR spectra of polymer VI*

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NMR spectra of polymer ~~III~~



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4. CONCLUSION

Novel polymers based on polyethylene glycol(400) and citric acid (10-30%) has been synthesized successfully.

The available surfactants are based mainly on acid slurry (linear alkyl benzene sulphonate) ,which is based on crude petroleum. In the present work we have used very small proportion of acid slurry (3-7%) and successfully used vegetable stock based polymeric surfactants as replacement of acid slurry. The compositions are ecofriendly and economical as they depend upon vegetable source polymers. Sorbitol in substantial quantity has been used which eliminate turbidity and transparent appearance and smooth feel to hands in washing preparation. The pollution causing chemicals like sodium tripolyphosphate is reduced. This is step towards replacement of petroleum product with green ecofriendly renewable product. Detergents give a very low surface tension thus they are expected to have better cleaning.

Normally we use 10-14% acid slurry in liquid laundry detergent compositions. Here we have used very small proportion of acid slurry (3to7%). and use of 10-14% of polymer does not practically harm the performance characteristics. In fact incorporation of polymeric surfactant gives excellent characteristics of foaming, surface tension and cleaning of stains of soil, tea, coffee and spinach. (See Table-4)

- 1) Our samples have been compared in all respects with commercial samples available in the market. Our samples stand up to the mark and some times perform better than commercial samples.
- 2) Our liquid Laundry detergents must be tried on pilot and commercial scale as they are technoeconomically viable compositions.

ACKNOWLEDGEMENT

The Authors are very thankful to Director LIT for Laboratory facilities, Director IIT, Pawai Bombay for recording IR and NMR spectra.

COMPETING INTERESTS

"Authors have declared that no competing interests exist."

AUTHORS' CONTRIBUTIONS

'Author A' designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. 'Author B' and 'Author C' managed the

analyses of the study. 'Author C' managed the literature searches..... All authors read and approved the final manuscript."

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398 **Table-1** **Composition of novel polymers based on polyethylene glycol.**

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Serial No.	Raw materials	Concentration (% by weight)		
		VI	A	B
1.	Sorbitol(70% solid)	75	80	60
2.	Polyethylene glycol(400)	05	10	30
3.	Citric acid	20	10	10

400 catalysts = 1% HCl, sodium metabisulphite =3.5%, sodium bisulphate =3.5%

401 Isopropanol =2% (as solvent)

402 **Table-2** **Composition of liquid detergents based on combination of neutralized**
 403 **acid slurry and novel polymer**

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Serial No.	Raw materials	Concentration (% by weight)			
		LA-1	LA-2	LA-3	LA-4
1.	Acid slurry	7	5	3	1
2.	S.L.E.S.	20	20	20	20
3.	Polymer	10	12	14	16
4.	Sorbitol	10	10	10	10
5.	Sodium sulphate	03	03	03	03
6.	Sodium	7.5	7.0	7.6	7.5

	carbonate				
7.	Perfume	0.5	0.5	0.5	0.5
8.	Distilled water	42.0	42.5	41.9	42.0
	Total	100	100	100	100

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S.L.E.S– sodium lauryl ether sulphate La- 1,2,3,4 - code for liquid detergents

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Table 3

PHYSICOCHEMICAL PROPERTIES OF THE SYNTHESIZED POLYMERS

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Serial No.	Polymer property	Observations		
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5.	Solubility in Water	Soluble	Soluble	Soluble
	Solubility in Xylene	Insoluble	Insoluble	Insoluble
6.	hydrophilic- lipophilic balance	15.19	11.32	11.43

7.	Flow time Ford cup No.4 in second at 30 ⁰ C	258	258	258
8	Surface Tension (in dyne/cm)By stalagmometer	27.5	24.20	19.07
9	% Oxirane oxygen(by HBr method)	3.77	2.9	3.71
10.	*Foam Volume(in cc)By cylinder method	900	950	800

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Table-4

Analysis of liquid detergents at 1% concentration by weight

Note: Surface tension of Distilled water=72.79 Dyne/cm

Detergent sample	Density(by density bottle)in g/cm ³	Surface tension(by stalagmometer)in dynes/cm	Foam height(by cylinder method)in cc	Flow time(by Ostwald's viscometer) in second
LA-1	0.9556	26.59	1000	180
LA-2	1.019	30.64	750	185
LA-3	1.003	26.59	1000	175

LA-4	1.019	34.01	800	165
Commercial	0.910	37.5	800	200

The pH of all samples was 8.5-9 at 1% concentration in distilled water

Table-5

Stain removal

Liquid detergents	Soil	Tea	Coffee	Spinach
LA-1	G	Ex	G	Ex
LA-2	G	Ex	G	G
LA-3	G	G	G	G
LA-4	P	P	G	P
Commercial	G	Ex	Ex	Ex

Abbreviation:

Ex (excellent) :90%, stain removed, G (good): 75%, stained removed, P(poor): 50%, stain removed.

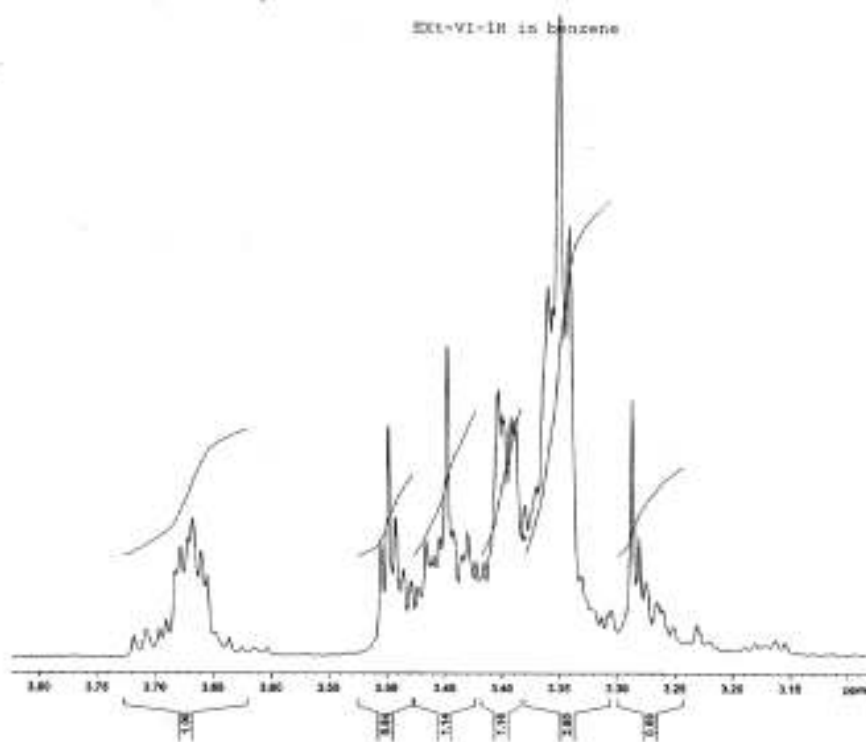
Fig.1 and Fig.2.

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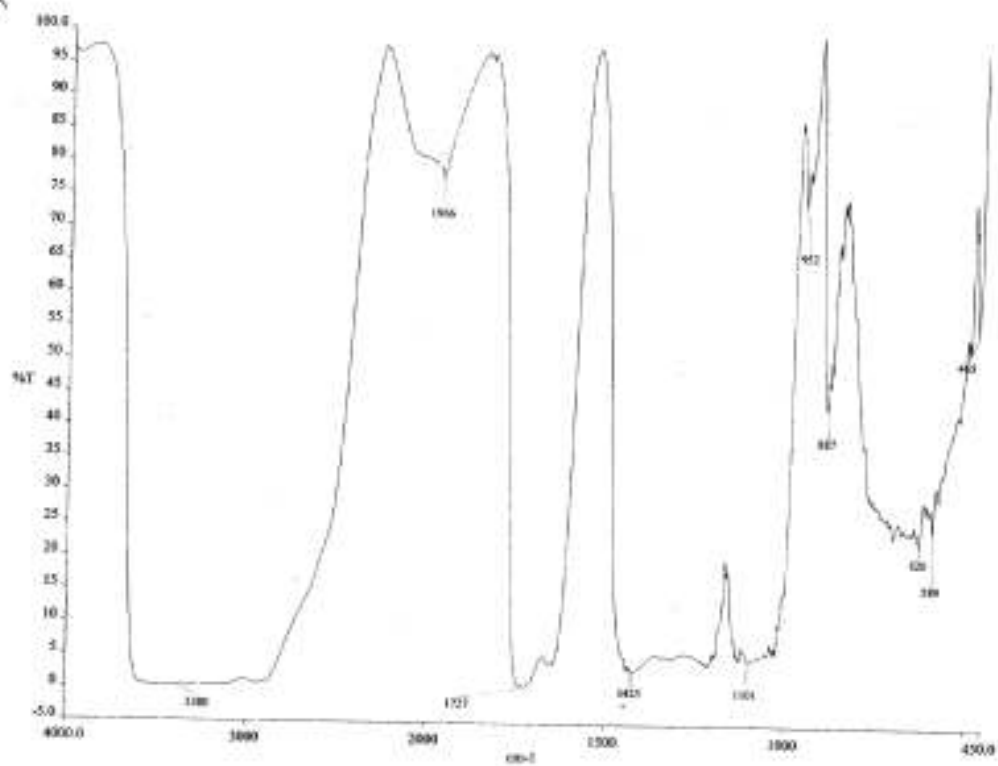
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NMR spectra of polymer ~~III~~

EXX-VI-1H in benzene



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476 the reference list and vice versa. In the text, citations should be indicated by the
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For Accepted, unpublished papers.

Same as above, but "In press" appears instead of the page numbers.

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557 **DEFINITIONS, ACRONYMS, ABBREVIATIONS**

558 Here is the Definitions section. This is an optional section.

559 **Term:** Definition for the term

560

561 **APPENDIX**