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# Eco friendly Novel Polymers based on Glycerol and Sorbitol as a Subtitutes of Acid Slurry in Detergents

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## Abstract

*Polymeric surfactants based on glycerol and sorbitol have been synthesized and used successfully in detergent compositions. In the present research work a small quantity of maleic anhydride, phthalic anhydride and citric acid along with major quantity of glycerol and sorbitol have been used in synthesis of polymers. The synthesized polymers have been analyses for their physicochemical characteristics like acid value, % oxirane oxygen, HLB ratio, cleaning efficiency and spectral properties like I.R. and N.M.R spectra. Selected novel polymeric surfactants based on these observations have been used in the preparation of powder detergent compositions. In progressive formulations acid slurry of petroleum origin has been replaced by novel polymer by 20-100 %. The total replacement of acid slurry with novel polymer is viable without affecting foaming, cleaning and stain removing capacity.*

**Keyword:** Glycerol, Sorbitol, Detergent, Polymeric surfactants.

## Introduction

The commercial powder detergents contain 20-25 % petroleum based active ingredients like acid slurry. The price of crude petroleum is quite high. The stock of crude petroleum is soaring year after year and hence it is important to develop bio-renewable agro-based alternatives for these conventional petroleum based surfactants.

As an alternative and permanent solution we must think of substitutes based mainly on glycerol and sorbitol which are of vegetable origin and can give eco-friendly products. In the present piece of research work a small quantity of maleic anhydride, phthalic anhydride, citric acid along and polyethylene glycol (400) with major quantity of glycerol and sorbitol have been used in synthesis of polymeric surfactant.

The objective is to replace 80-100 % acid slurry with novel polymer. The mole ratio of the ingredients and concentration of catalyst have been standardized to get polymer of desired acid value and cleaning capacity. Acid slurry has been successfully replaced by 20-100% in several powder detergent compositions by using novel polymer. These compositions have been prepared and analyses for foam, surface tension and stain removing properties. These properties were compared with standard brand of commercial detergents. Spectroscopic analysis like I.R and N.M.R help to show that presence of functional groups like acids, alcohol, ether and esters in polymers.

## Material and Methods

**Experimental** The synthesis of desired polymers has been carried out in a four neck round bottom glass reactor of 2 liter capacity. A stirrer with speed regulator was inserted through the central neck of the reactor. Through the right neck of the reactor a thermometer with accuracy of ± 1 $^{o}$C was inserted. The third opening of the reactor was used for addition of reactants. Exactly weighed quantities of various ingredients were introduced into the reactor. Thereafter the heating was commenced slowly and steadily to attain the temperature of 120-130$^{o}$C in about 90 minutes in an electric heating mantle with temperature controlling regulator (± 3$^{o}$C). Heating was continued for three hours and then the total reactor mass was cooled to 80$^{o}$C. The prepared polymer samples were then stored in tightly corked bottles. These Polymer samples were systematically analyzed for their acid value, viscosity, H.L.B, pH and % oxirane oxygen value by standard laboratory methods[1-6]. They were also analyses by I.R.[7], N.M.R[8] spectroscopy to know the finger print of ester group, ether group, free-OH groups and free acid groups.

**Preparation of Powder Detergent** Composition of various ingredients used in the preparation of detergent powder are shown in the formulations table-3. The said ingredients in the powdered form are weighed and mixed thoroughly in a tray. Then the liquid ingredients like acid slurry, sodium lauryl ether sulphate (S.L.E.S), and polymer were added. This mass was then homogenized thoroughly in a homogenizer pot and the homogeneous mass thus obtained was packed in plastic pouches.

The surface tension of powder detergents solution was measured using stalagmometer (for 1%, 0.5% and 0.25% concentrations). Foam was measured by using mechanical agitation in a closed glass cylinder of 1 L capacity.

**Analysis and Testing of Powder Detergent[9,10,11]: Stain Preparation** The soil medium having following composition by weight, Carbon black (28.4%), Coconut oil (35.8%), Lauric acid (17.9%), Mineral oil (17.9%) was prepared. The mixture of carbon black and lauric acid along with mineral oil was taken in a pastel mortar. Coconut oil was then added slowly to from a thick paste. All the components were ground in the pastel mortar for 1-2 hours till a finely grounded mixture was obtained. The fine grinding is indicated by smooth feel of the paste medium.

Soil solution was prepared by adding 2 g of above soil medium paste in 500 ml of carbon tetrachloride for staining cloth sample. The solution after preparation was kept in packed bottles.

**Tea Stain Solution:** This was prepared with following composition. Tea (Taj Mahal) (2.2 %), Sugar (8.0 %), Milk (38.4 %) and Water (51.4 %). 25 g of Water was warmed to 35 to 40 $^{o}$C and tea powder and sugar were added to it. The contents were further warmed till the solution starts boiling and at this stage milk was added and heating was continued at boiling temperature of the mixture for further 5 minutes. The prepared tea was passed through a tea filter and was used as tea medium for staining the clothes.

**Preparation of Coffee Medium:** This was prepared with composition of Coffee (1%), Sugar (8.1%), Milk (51.9%), Water(39 %). 25g of milk and water were taken in a beaker and the contents were warmed initially to a temperature of 35 – 45 $^{o}$C before adding the coffee powder and sugar. The heating was continued and the mixture was allowed to boil for about 5 minutes. The prepared coffee was passed through a coffee filter and was used as coffee medium for staining the clothes.

**Preparation of Palak (Spinach) Medium:** This medium had the composition of Oil (1.34%), Spinach (9%) and Water (89.66%). Oil was heated in a pan and spinach was added to it and fried for about 5 minutes. Half cup of water was then added to the contents and the mixture was cooked for about 10 minutes. After preparation it was stored in tight bottle. This preparation was used as spinach medium for staining the clothes.

**Method of application of Soil:** The cloth pieces of size 24 x 32 cm$^2$ were prepared. 50 ml of soil solution was taken in a beaker and the cloth sample was dipped in it for 5 minutes. Thereafter the cloth piece was kept outside for drying in open atmosphere for 2 hours. After drying the cloth was cut into small size of 6x8 cm samples which were then used for washing.

**Method of application of (Spinach, Tea and Coffee) stains:** The stains of spinach, tea and coffee mediums were applied at the centre of cloth samples of 6x8 cm$^2$ size by using pipette. The stain applied was distinctly visible. The cloth sample was then kept in an oven at 55-60 $^{o}$C for about 15 min and used for testing.

**Method of Washing[12,13]:** The solutions of different concentrations of detergent powder (1%, 0.5% and 0.25%) were prepared. Heat these solutions to temperature of 60$^{0}$C. Dip soiled cloth sample in it for 5 minutes and give to and fro 10 hand washes. Allow it to dry and visualized the effect on stain.

## Results and Discussion

Table-1 gives composition of various polymers designed specifically for use in detergents. The main common feature of all polymers is the use of 90 % ecofriendly chemicals that can be derived from vegetable sources like glycerol and sorbitol. All polymer samples contain small proportion of polyethylene glycol (400) which helps for better solubility and increased stain removing properties. In all compositions a small proportions of acids like maleic, phthalic and citric acid have been added.

**Table- 1**
**Composition of novel polymers**

| Sr. No | Polymer (ingredients in weight %) | G17 | G18 | G19 |
|---|---|---|---|---|
| 1 | Glycerol | 80 | 80 | 80 |
| 2 | Polyethylene glycol (400) | 5 | 5 | 5 |
| 3 | Sorbitol | 10 | 10 | 10 |
| 4 | Maleic anhydride | --- | 5 | --- |
| 5 | Phthaleic anhydride | 5 | --- | |
| 6 | Citric acid | --- | --- | 5 |

Note 2.5% $NaHSO_3$, 2.5% $NaHSO_4$ and 1% Conc. HCl used as catalyst in all batches.

These acids help in enhancing cleaning capacity of polymers prepared. The catalysts used, namely sodium bisulphate, sodium bisulphate and hydrochloric acid promotes esterification reaction.

**Table-2**
**Physicochemical analysis of polymers**

| Sr. No. | Polymer | G17 | G18 | G19 |
|---|---|---|---|---|
| 1 | Density (g/cc) | 1.02 | 1.02 | 1.03 |
| 2 | % solids | 93.27 | 92.09 | 92.40 |
| 3 | pH (1% solution) | 3.85 | 3.80 | 4.29 |
| 4 | Acid value | 21.5 | 24.26 | 17.31 |
| 5 | Foam Volume(cm$^3$) | 100 | 100 | 100 |
| 6 | Viscosity ( Seconds-by ford cup NO-4 at 30$^0$c) | 185 | 190 | 200 |
| 7 | H.L.B Ratio | 17.8 | 17.9 | 17.8 |
| 8 | % Oxirane oxygen | 3.72 | 4.12 | 4.16 |

The physicochemical analysis of polymers is given in table-2. The % solids indicate that all samples have 92-93.27% solids in final polymer samples. The pH of polymers (1% solution) is 3.8-4.29. The acid values of polymers show that all samples have some free acid groups. Prepared samples also have excellent viscosity of 185-200 seconds.

The composition of powder detergents based on polymer G18 is given in table-3.

All sample have an alkaline pH and give excellent foaming characteristics, Surface tension and stain removing properties for stains of soil, tea, coffee and spinach (palak). These samples are not only comparable but at times better than available commercial products in the market as shown in table-4.

The physiochemical analysis like foam, surface tension of powder detergent is given in table-5.

FT-IR spectroscopy shows presence of ester group (1720.93), ether group (1105.89), Free-OH groups (3304.47) and free acid groups (2886.56). N.M.R. spectra of polymer shows presence of ester group and confirm the reaction between alcoholic OH group and carboxylic acid group. Presence of ether group indicates the condensation of OH groups to from polymeric linkages. The peaks at 4.71 ppm are due to ester linkage as given in figure-1 and 2.

**Table-3**
**Compositions of powder detergents**

| Sr. No. | Ingredients in weight % | G18PD1 | G18PD2 | G18PD3 | G18PD4 |
|---|---|---|---|---|---|
| 1 | Acid Slurry | 8 | 5 | 2 | --*--- |
| 2 | Polymer | 2 | 5 | 8 | 10 |
| 3 | S.L.S (40% Solids) | 3 | 3 | 3 | 3 |
| 4 | S.L.E.S(30% solids) | 5 | 5 | 5 | 5 |
| 5 | Salt | 15 | 15 | 15 | 15 |
| 6 | Sodium Carbronate | 30 | 30 | 30 | 30 |
| 7 | Sodium Sulphate | 1.5 | 1.5 | 1.5 | 1.5 |
| 8 | Dolomite | 35 | 35 | 35 | 35 |
| 9 | $TiO_2$ | 0.5 | 0.5 | 0.5 | 0.5 |

Sodium lauryl ether sulphate (S.L.E.S), sodium lauryl sulphate(S.L.S).

**Table-4**
**Cleaning analysis of powder detergents**

| Concentration | Sample | Stain medium | | | | Total Points |
|---|---|---|---|---|---|---|
| | | Soil | Coffee | Tea | Spinach | |
| 1% | G18PD1 | 3 | 3 | 3 | 3 | 12 |
| | G18PD2 | 3 | 3 | 2 | 3 | 11 |
| | G18PD3 | 3 | 3 | 3 | 3 | 12 |
| | G18PD4 | 3 | 3 | 3 | 3 | 12 |
| | CDP | 3 | 3 | 3 | 3 | 12 |
| 0.5% | G18PD1 | 3 | 3 | 3 | 2 | 11 |
| | G18PD2 | 3 | 3 | 2 | 3 | 11 |
| | G18PD3 | 3 | 3 | 3 | 3 | 12 |
| | G18PD4 | 3 | 3 | 3 | 3 | 12 |
| | CDP | 3 | 3 | 3 | 3 | 12 |
| 0.25 % | G18PD1 | 3 | 3 | 2 | 2 | 10 |
| | G18PD2 | 2 | 2 | 2 | 2 | 8 |
| | G18PD3 | 2 | 3 | 2 | 2 | 9 |
| | G18PD4 | 3 | 3 | 3 | 2 | 11 |
| | CDP | 3 | 3 | 3 | 2 | 11 |

Cleaning Points - 0 - No Cleaning, 1-25% Cleaning, 2- 50 % Cleaning, 3- 75 % Cleaning, 4- 100% Cleaning, CPD-Commercial Detergent Powder

**Table-5**
**Physicochemical analysis of powder detergents**

| Concentration | Sample | Foam Volume ($cm^3$) | | | | Surface Tension (dyne/cm) |
|---|---|---|---|---|---|---|
| | | 0min | 5min | 10min | 15 min | |
| 1% | G18PD1 | 1000 | 970 | 950 | 950 | 24.60 |
| | G18PD2 | 1000 | 950 | 940 | 930 | 24.92 |
| | G18PD3 | 1000 | 950 | 940 | 920 | 26.10 |
| | G18PD4 | 1000 | 930 | 920 | 900 | 29.46 |
| | CDP | 1000 | 960 | 960 | 940 | 24.12 |
| 0.5% | G18PD1 | 900 | 870 | 870 | 850 | 26.24 |
| | G18PD2 | 900 | 870 | 850 | 830 | 27.86 |
| | G18PD3 | 890 | 860 | 850 | 830 | 27.25 |
| | G18PD4 | 870 | 850 | 820 | 800 | 30.91 |
| | CDP | 900 | 900 | 870 | 850 | 26.62 |
| 0.25% | G18PD1 | 780 | 780 | 760 | 760 | 27.93 |
| | G18PD2 | 750 | 740 | 740 | 720 | 29.46 |
| | G18PD3 | 710 | 700 | 680 | 670 | 30.02 |
| | G18PD4 | 580 | 570 | 560 | 540 | 31.90 |
| | CDP | 800 | 780 | 750 | 750 | 30.10 |

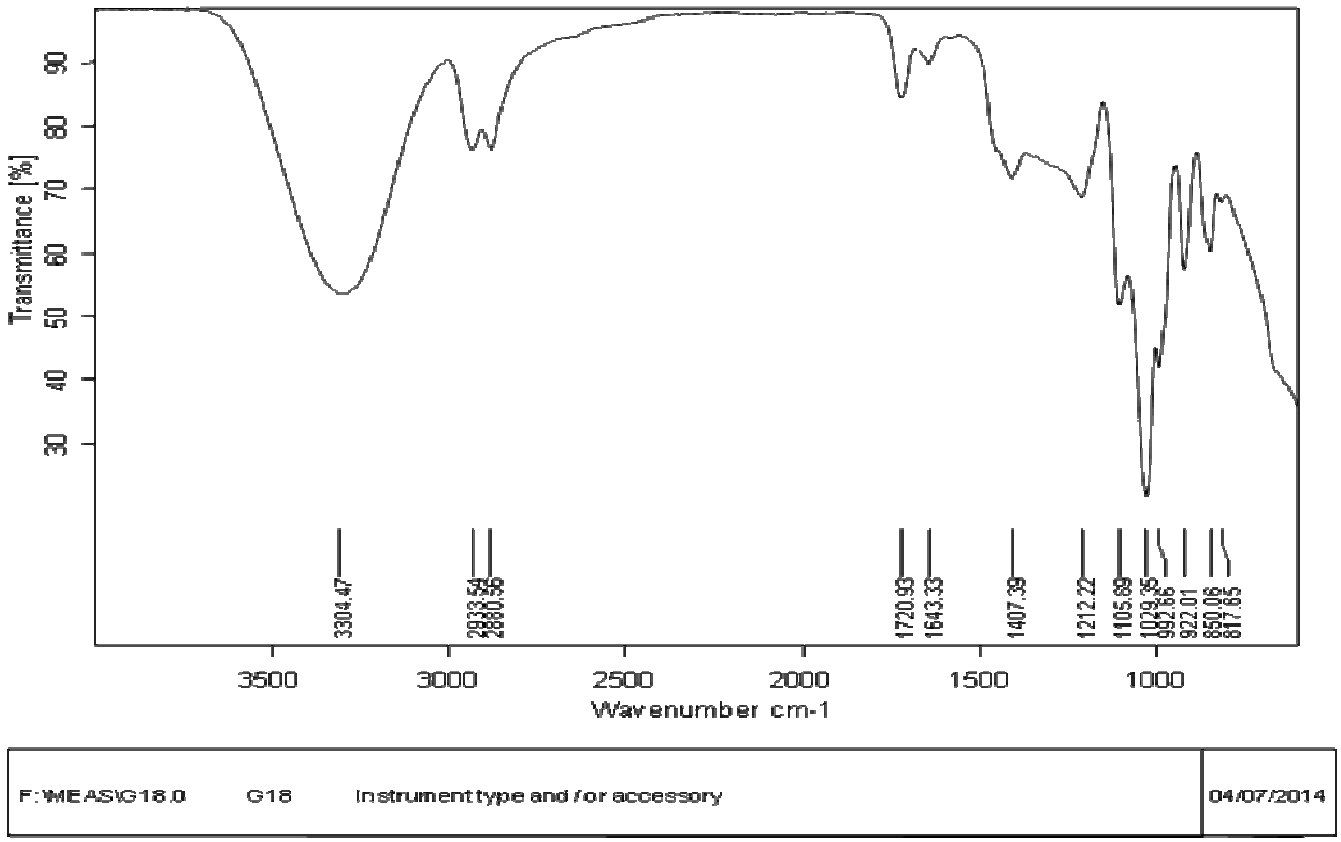


**Figure-1**
**Spectroscopic analysis of polymer G18 Ft-IR Analysis of polymer G18**

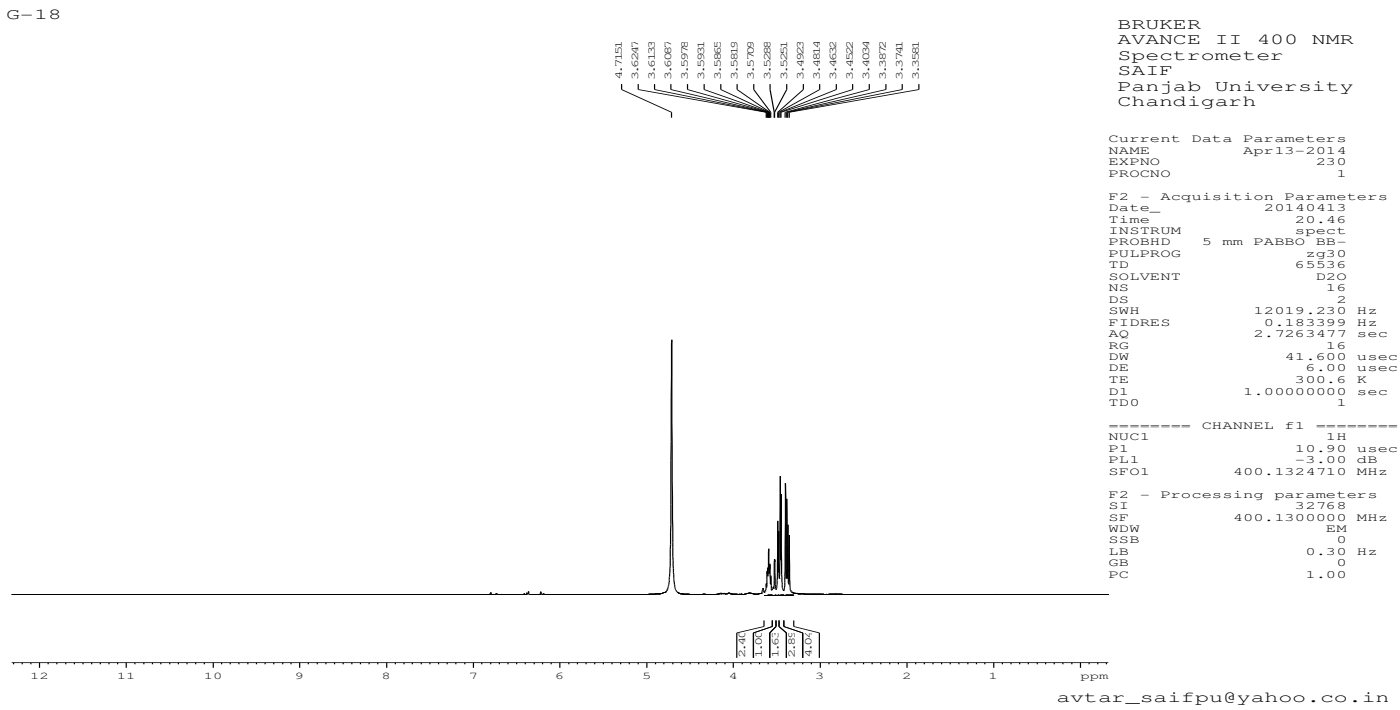


**Figure-2**
**N.M.R Analysis of polymer G18**

## Conclusion

Glycerol and Sorbitol based polymeric surfactant can be used successfully for formulation of powder detergent. A combination of organic acids like maleic anhydride, phthalic anhydride, citric acid and polyethylene glycol (400) in polymer give excellent properties for detergent formulations. Particularly use of maleic anhydride helps to improve stain removing capacity.

In our compositions we have successfully replaced 70-100% acid slurry with novel polymer. The viscosity of polymer is reasonable (185-200sec) which helps in easy handling and mixing with ingredients. H.L.B ratios strongly suggest the use of these polymers in detergent combinations. A high percentage of oxirane oxygen value shows the water affinity and possible cleaning efficiency of the polymer as a detergent component.

The composition of powder detergents is shown in table-3. A small proportion of sodium lauryl sulphates, sodium lauryl ether sulphate have been used in all formulations to boost foaming and detergent properties. The proportion of other ingredients is kept constant in all formulations. The Titanium dioxide gives good whitening effect on cloths.

The surface tension, foaming characteristics of different samples at concentrations 0.25-1 % is recorded in table-4 and 5. A commercial powder detergent was analyzed simultaneously to know the practical utility and performance of our powder detergents. The lowering of surface tension at all concentrations (0.25-1%) is excellent and is comparable with commercial sample. lowering of surface tension is one of the basic requirement for getting good cleaning and stain removing properties. The foaming characteristic of all samples are satisfactory and comparable with commercial sample at all concentrations.

The stain removing characteristics for stains of soil, coffee, tea, spinach are very good at all concentrations. The powder detergent combination G18PD4 give excellent cleaning capacity, foam and surface tension as compared to commercial powder detergent. The synthesis of polymers and formulation of powder detergents must be tried on pilot and commercial scale.

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