EXPERIMENTAL
MATERIALS AND METHODS

In this chapter, first, different raw materials required for the synthesis of polystyrene glycol, its blends, esters and copolymers have been described and then, various techniques of testing and evaluation of the product are described.

3.1. MATERIALS

Different types of materials used and their purification are given below:

Styrene

Styrene monomer, used for the synthesis of polystyrene glycol was purified in the following manner:

150 ml of styrene (Johnson grade) was initially mixed with 100 ml of 4 percent sodium hydroxide in a separating funnel for about 10 minutes. The styrene layer became yellowish. The colourless sodium hydroxide containing impurities was removed. This process was repeated ten times. This was then followed by washing of monomer with 100 ml of distilled water till there
were no traces of alkali in the washings. This was tested with litmus paper and phenolphthalein solution. Approximately 140 ml of washed styrene monomer was kept overnight in a conical flask which had anhydrous sodium sulfate as a dehydrating agent. The washed styrene was subjected to the vacuum distillation. The flask was completely covered with cotton and the receiver was kept in ice. This receiver was connected to the vacuum pump. Styrene started distillation at 30°C. The first fraction of about 15 ml was rejected and second fraction of about 50 ml was collected. The remaining last fraction of about 10 ml was also rejected. The 50 ml of middle fraction styrene was stored in a cool place and used when desired.

At the time of use, styrene was tested by adding methyl alcohol in about 10 ml styrene. No precipitate was formed which showed that styrene is monomeric.

Benzoyl peroxide

Benzoyl peroxide (LR grade) was used as catalyst in the synthesis of polystyrene. It was freshly recrystallized before use according to procedure described by Vogel. Benzoyl peroxide was dissolved in chloroform at room temperature and precipitated by adding twice the volume of absolute methyl alcohol.
Calcium oxide

It was obtained from local market and used as catalyst for monoglyceride formation without further purification.

Oils

Alkali refined linseed, nigerseed and castor oils were used in the preparation of oil modified alkyds. Refining of oils was done as follows:

Acid value of the commercial oil was determined and then 16° Baume solution of required sodium hydroxide (for 16° Baume, 10.97 percent sodium hydroxide required at 15°C) was prepared by taking 5 percent excess of sodium hydroxide. Oil was heated to 50°C and sodium hydroxide solution of 16° Baume was added within 20 minutes into heated oil with rapid stirring (55 r.p.m.). Temperature was raised to 60°C to 70°C and stirring was slowed down (so that only oil could move). This was continued for another 20 minutes. Mixture was kept overnight so that large flakes (lumps) of soap were settled down. Next day, oil was decanted in the another beaker and lower portion of soap was rejected. Hot water was added into oil on sides of beaker and then lower layer of water was removed by siphon. This process was repeated for 4 times. Again water was added and mixture
was stirred and soap was removed. Procedure was repeated until whole of soap was removed from the oil. This was tested by adding phenolphthalein in the last traces of washing, until no pink colour was developed. Oil was dried by adding anhydrous sodium sulfate. Acid value of refined oil was determined which was less than one. In case of castor oil refining, 8 percent sodium chloride solution was also used.

Dehydrated castor oil

Dehydrated castor oil having an acid value of 6 and viscosity of 2 poise was used along with linseed oil and nigerseed oil (taken in a weight ratio of 1:3) for preparation of conventional styrenated alkyds.

Linseed fatty acids

Linseed fatty acids were used as monobasic acids for esterification of polystyrene glycol. They were obtained by splitting of linseed oil as follows:

100 parts (by weight) of oil was saponified by adding 30 parts (by weight) of potassium hydroxide, dissolved in about 500 parts of ethyl alcohol. The solution was boiled freely
under reflux condenser for 1 to 2 hours. The reaction was completed when no globules of oil were present if a few drops of the mixture was mixed with a little water. After that, most of the alcohol was removed by distillation. The soap was dissolved in water and converted into the free fatty acids by adding dilute sulfuric acid.

Phthalic anhydride

BDH, LR grade was used in the preparation of alkyd resin and copolymers. Suspected phthalic acid was removed by mixing with cold chloroform. In this case, phthalic anhydride dissolved readily, but the acid was insoluble.

Glycerol

BDH, LR grade was used without further purification in all esterification reactions, i.e., in the preparation of alkyds, ester gum and copolymers.

Rosin

WW grade was used in the preparation of various esters of rosin. Rosin had an acid value of 170.
Driers

Lead and cobalt naphthenates were used as driers for alkyds, blends, styrenated alkyd, copolymers and oleoresinous varnishes of drying oil. Metal content of lead naphthenate was 25 percent, while that of cobalt naphthenate was 7-9 percent. 0.3 and 0.03 percent lead and cobalt naphthenates were added as metal to resin in case of alkyd resins, styrenated alkyd and copolymers. In case of oleoresinous varnishes, driers added were based on a percentage of metal to oil. In general, the combination of two or more metals was preferred, because each had a specific action in the drying process. Lead was usually considered to be a "through" drier and cobalt a "surface" drier.

Potassium hydroxide

LR grade was used for saponification of benzoate end groups of polystyrene into polystyrene glycol and for splitting of linseed oil.

Formaldehyde

37 percent formaldehyde solution in water known as formalin was used for preparation of urea-formaldehyde resin.
Urea

LR grade was used for preparation of urea-formaldehyde resin.

Benzene

Benzene of LR grade was used as a solvent for dissolving polystyrene and polystyrene glycol and was made free from thiophene present as impurity by shaking with concentrated sulfuric acid\textsuperscript{115}.

Toluene

Toluene was used as solvent and was made free from sulfur compound like methyl thiophene (thiotoluenes) which was present as an impurity by shaking several times with about 10 percent of its volume of concentrated sulfuric acid\textsuperscript{116}. In this case, temperature control was necessary because of greater ease of sulfonation of toluene itself.

Pyridine

Pyridine, AR grade was used as a reagent in the determination of hydroxyl value. It was made perfectly dry by
refluxing it over potassium hydroxide pallets. It was carefully distilled. Pyridine fraction of boiling point above 114°C, i.e., 115.5°C was used for preparation of acetylation mixture.

Acetic anhydride

BDH, LR grade of boiling point 135°C-140°C was used without further purification for preparation of acetylation mixture during determination of hydroxyl value of polystyrene glycol.

Xylene

BDH, LR grade of boiling point 137°C to 138°C was used as solvent without further purification.

n-Hexane

LR grade of boiling point 67°C-70°C was used as solvent for various esters of polystyrene glycol.

Methyl ethyl ketone

LR grade of boiling point 79.5°C was used as solvent without further purification. It was used as a solvent because
it had properties similar to those of acetone but it had some
what higher boiling point and was therefore less inflammable.

Chloroform

BDH, LR grade of boiling point 61°C (free from ethyl
alcohol, which was used as a stabilizer) was used without further
purification. It was placed in dark to avoid the photochemical
formation of phosgene.

Methyl alcohol

BDH, LR grade was used without further purification as a
non-solvent for precipitation of polystyrene and polystyrene glycol
from their benzene solution.

Ethyl alcohol

Commercial rectified spirit was taken and purified. It
was used in determination of hydroxyl value and acid value of
polystyrene glycol and different resins prepared. Details of
the purification of rectified spirit are as follows:

3 g of potassium hydroxide was dissolved in some
rectified spirit. A solution of 1.5 g silver nitrate, prepared
in distilled water was added in one litre spirit. Now, potassium hydroxide solution prepared in alcohol was added into it. A black precipitate was developed. Solution was kept overnight and then distilled. Vapours of ethyl alcohol (95 percent was passed over calcium oxide and then collected.

n-Butyl alcohol

BDH, LR grade of boiling point 116°C was used without further purification in determination of hydroxyl value and in preparation of butylated urea-formaldehyde resin.

1,4-Dioxane

BDH, LR grade of boiling point 101.5°C was used as solvent for dissolving polystyrene having benzoate end groups. It was miscible with water in all proportion. It was used as solvent because its action was similar to that of ether but more pronounced.

Besides this, sodium hydroxide (LR grade), sodium carbonate (LR grade) were used as alkali and hydrochloric, sulfuric and nitric acids were used as acids for testing of samples.
3.2. METHODS

Techniques used for characterization and evaluation of products prepared are described in this part. Details of these methods are described under following 3 headings.

(A) Physical testing
(B) Analytical method
(C) Evaluation of film properties

3.2.A. Physical testing

This includes the determination of softening point of polystyrene glycol and its esters by capillary method and relative viscosity by using Ostwald U-tube viscometer. Inherent viscosity was calculated from the formula:

\[ \eta_{\text{inh}} = \ln \frac{\eta_{\text{rel}}}{C} \]

where \( \eta_{\text{rel}} \) = relative viscosity and \( C \) is the concentration of product in g/100 ml of solvent at 25°C.

3.2.B. Analytical method

Here, the determination of hydroxyl value of polystyrene glycol and acid value of all the samples of alkyds, mixed esters and copolymers have been described.
(i) **Determination of hydroxyl value** - "Hydroxyl value is the number of milligrams of potassium hydroxide required to neutralize the acetic acid capable of combining by acetylation with one gram of the sample". Hydroxyl value is equivalent to the hydroxyl content of the material based on the weight of the unacetylated sample. The process consists in acetylating the sample with a measured quantity of acetic anhydride in pyridine, decomposing the excess anhydride by boiling with water and then, after the addition of sufficient butyl alcohol to give a homogeneous solution, titrating with alcoholic alkali. A control test with the acetic anhydride and pyridine without the sample provides a measure of the acetic anhydride available for acetylation; a similar test with the sample and pyridine without the acetic anhydride provides a measure of the free fatty acid present. From the figure obtained, the acetyl value or hydroxyl value of the sample is calculated. Details of the procedure are as follows:

0.5 to 3.0 gram of the sample was accurately weighed in 250 ml round bottom flask. 5 ml of pyridine-acetic anhydride mixture (prepared by adding one volume of acetic anhydride and seven volume of pyridine) was added into the flask and refluxed for 1 hr. Flask was cooled to 50°C and 5 ml of distilled water was added from the top of the condenser tube. Mixture was
shaked well and boiled for 5 to 10 minutes. Flask was then cooled and condenser was washed with 30 ml of butyl alcohol. The content of the flask was titrated against 0.35N alcoholic sodium hydroxide solution in the presence of few drops of phenolphthalein as indicator.

Same operations were carried out with 5 ml of pyridine-acetic anhydride mixture alone and also with corresponding weight of the sample plus 5 ml of pyridine. Hydroxyl value was calculated from the following formula:

\[
\text{Hydroxyl value } H = \frac{56.1 \times N \times Y}{W}
\]

where \(N\) = Normality of sodium hydroxide solution

\(Y\) = Volume of sodium hydroxide in ml corresponding to the amount of acetylated sample formed = \(a + b - c\)

where \(a, b, c\) are respectively the volume in ml of sodium hydroxide required by blank with pyridine-acetic anhydride mixture; sample plus pyridine, and sample plus pyridine plus acetic anhydride.

\(W\) = Weight in g of the sample taken for the test.
(ii) **Determination of acid value** - "Acid value is the number of milligrams of normal potassium hydroxide solution required to neutralize the free acid contained in one gram of the sample."

In order to determine acid value, a known weight of the material was dissolved in a neutral solvent mixture of benzene and ethanol (1:1) and titrated against standard potassium hydroxide using phenolphthalein as indicator. The details are as follows:

1 to 2 gram of sample was weighed accurately into the flask and 25-30 ml of neutral solvent mixture was added into the content of the flask. Sample was dissolved completely by refluxing on a water bath. This was titrated against standard potassium hydroxide solution to the appearance of light permanent pink colour. Volume (in ml) of the standard potassium hydroxide solution used was noted and the acid value was calculated from the formula:

\[
\text{Acid value (as mg of KOH/g sample)} = 56.1 \times \frac{V \times N}{W}
\]

where \( V \) = volume in ml of standard potassium hydroxide solution used.

\( N \) = Normality of the standard potassium hydroxide solution

\( W \) = Weight in g of the material taken for the test.

3.2.C. Evaluation of film properties

All samples of blends, oleoresinous varnishes and copolymers were evaluated for their use as film former in surface
coating industry. They were tested according to Indian Standard Specification no. 1S:101-1964 and 1S:197-1969 for drying characteristics, scratch hardness, flexibility and adhesion and resistance towards water, acids, alkalies and solvents. Tin and glass panels of 15 cm X 5 cm were used for specific tests. All the samples were thinned with suitable solvents to brushable consistency and applied to panels after adding driers or amino resins and dried or cured as the case was.

(i) Drying characteristics - Linseed oil based alkyds, blends, copolymer and oleoresinous varnishes were air-dried and their drying time, i.e., surface-dry, hard-dry and tack-free times were noted. Surface-dry is that condition of the varnish film, in which, when clear, dry sand was sprinkled on the surface of the film and allowed to remain for about 10 seconds, it could be removed without injury to the film by a hair brush. In hard-dry condition, a second coat of the sample could be applied satisfactorily on the film after slight rubbing down. In order to examine the tack-free times of the varnish film, panels was placed in one pan of a suitable balance and was counterpoised with weights. A further weight of 2.5 kg was placed and varnish surface of the panels was pressed with thumb till the two pans were balanced. It was hold for one minute and then slowly
released. There would be no sign of tackiness to the thumb. Nigerseed oil and castor oil based samples of alkyds, blends and copolymers were baked after mixing with butylated urea formaldehyde resin at 100°C, 110°C, 120°C, 130°C, 140°C and 150°C for 10, 20, 30, 40 minutes till an optimum condition was obtained to get a smooth film.

(ii) **Scratch hardness** - Scratch hardness of the films of all samples of alkyds, blends, esters and copolymers was determined. In scratch hardness, resistance to scratching under a specified load, of the dried film of the varnish was tested. Mechanically operated "Sheen" scratch hardness tester was used to determine scratch hardness of the film. For this test, tin panels were dried in the horizontal position for 48 hours under specified drying conditions or stoved as the case was.

Scratch hardness of the dried film was measured on tin panels with mechanically operated "sheen" scratch hardness tester by placing increasing load over a hardened needle which moves on the film. Scratch hardness (maximum load in gram) of samples were determined in each case. In this case, a scratch, showing the bare metal should not be produced.
(iii) **Flexibility and adhesion** - Quarter inch mandrel was used for testing flexibility and adhesion of the sample on tin panels. The test was carried out by bending the tin panel in 1/4" mandrel. The varnish film is bent through 180° after specified period with the film outside and examined for any damage, detachment or cracking of the film. For this test, panels were air-dried for 96 hours (4 days). In this test, care was taken that time of bending should not exceed one second. The film shall not become visibly damaged or detached.

(iv) **Water resistance** - All the samples were allowed to air-dry in a horizontal position for 48 hours. The sides of the glass panels were protected by wax. The panels were immersed in distilled cold water at room temperature for 48 hours. After that, panels were taken out and washed with running fresh water and air dried. The dipped portion was examined after four hours for appearance, i.e., loss of gloss, change in colour and for other visible damages. The condition of the film were recorded and panels were further immersed in water, to determine maximum water resistance in each case.

The films were also tested for boiling water resistance. Panels were placed in boiling water and condition of films was recorded after every 2 hours as described above.
(v) **Acid resistance** - For this test, the glass panels of all samples were prepared as described above and sides of the glass panels were protected by wax. Panels were immersed in 2 percent (v/v) solutions of hydrochloric, sulfuric and nitric acids separately at room temperature (25°C). Panels were taken out after 24 hours washed in running fresh water, allowed to air dry for an hour. The dipped portion of the films were examined for appearance, i.e., loss of gloss, change in colour and for any sign of disintegration or visible damages.

In order to find maximum resistance in each acid, panels were further immersed in their respected acid solution and films were checked at a regular interval of 24 hours.

(vi) **Alkali resistance** - For this test, the glass panels of all the samples were prepared as described above and immersed in 2 percent solution of each of sodium carbonate and sodium hydroxide separately at ambient temperature (25°C).

Panels were taken out after half an hour and washed in running fresh water and dried for an hour. Condition of the film was observed in respect of loss of gloss, change in colour, cracks, or sign of visible damages, etc. After recording the condition of the film, panels were further immersed in respected
solutions. Condition of the panels dipped in sodium carbonate was checked at a regular interval of 5 days. Whereas, those immersed in sodium hydroxide was checked after each half an hour in the same manner as described above.

(g) **Solvent resistance** - Glass panels were prepared and sides of panels were protected by wax. Panels were immersed in hydrocarbon solvents namely xylene, white spirit, petrol and 1:1 mixture of xylene and toluene, separately at ambient temperature (25°C) for 5 minutes only. Panels were taken out and allowed to stand in a vertical position for 5 minutes and then rubbed with cotton wool soaked in respected solvents. Condition of the film was examined for any sign of permanent injury.