GENERAL INTRODUCTION

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In everchanging world the 'Time' demands for materials having desirable chemical, mechanical and electrical characteristics and that finds application on large scale or exhibit potential for unprecendented technological utility. The impact of this underscored truth have vividly directed the attention of investigators to polymeric system.

In recent times, the evergrowing vista of applicability of ION-EXCHANGE RESINS in various field such as analytical and preparative chemistry, pharmacy and industry, stimulated a rush for finding new ION-EXCHANGE RESINS.

1.1 ION-EXCHANGE RESINS:

These are synthetic organic ion-exchange materials prepared by the incorporation of appropriate functional groups into polymeric structures. The structure may be based upon polystyrene and divinylbenzene, phenol and formaldehyde, or similar stable polymeric chemical structures. To function as a cation exchanger the resin is substituted with either sulfonic acid groups (for strong cation exchangers) or carboxylic acid groups (for weak cation exchangers). Anion exchangers are obtained by introducing primary and secondary amino groups into the polymeric lattice.

The first use of ion-exchangers was more than a century ago, and until the introduction of the synthetic ion-exchange resins in 1935 the inorganic naturally occuring zeolites were used for ion exchange studies and water softening. The first synthetic ion exchangers were prepared in 1935 using a phenol - formaldehyde polymer for the cation exchanger and a phenylenediamine-formaldehyde polymer for the anion-exchanger. More recent advances in this field include the development of chelating resins and amphoteric ion-exchange resins.

1.2 ION-EXCHANGER:

Ion-exchangers are solid and suitably insolubilized high molecular weight polyelectrolytes possessing labile or mobile ions which can exchange their mobile ions for ions of equal charge from the surrounding medium, without altering the general physical nature of the ion-exchanger. These ions are cations in a cation exchanger and anions in an anion-exchanger. Thus it can be seen that a cation exchanger consists of a polymeric anion and labile cations, and an anion exchanger of a polymeric cation and labile anions.

Ion-exchanger may be defined as the reversible interchange of ions between a solid phase (Ion-exchange material) and a liquid phase in which there is no permanent change in structure, "Reversible" and "no permanent change" are the key points in this definition. However, a study of ion-exchange, either in laboratory or in the literature, shows that the use of ion-exchange material extend considerably beyond this definition.

Viewed in a different light, ion exchangers can be considered high molecular weight acids or bases with a high molecular weight cation, which can exchange their hydrogen or hydroxyl ions for equally charged ions and thus are converted into high molecular weight salts. If such a solid acid is neutralized with a base into the salt, however, the cations bound to the polyelectrolytes can again be displaced by other cations. The resulting process is known as cation exchange and the polyelectrolyte is the cation exchanger. In the second case, a solid base is obtained which is capable of OH^- exchange and can be neutralized with an acid, and the anion which was bound first can again be displaced by another anion - a process then known as anion exchange. The polyelectrolyte taking part in this process is called the anion exchanger.

Since the exchange groups are hydrophilic and resin matrix with such groups are soluble in water, and as the groups are attached to the polymeric exchanger structure, they tend to draw the whole exchanger into solution also. To prevent this the polymer structure in the synthetic resins is held together with cross-linkers in order to form a three dimensional molecule, while a type of crosslinking of a somewhat similar nature exists in the natural materials. These cross-linkers restrain the tendency of the resin to dissolve.

For practical purpose the desirable characteristics of an ion-exchanger are that it should provide an insoluble chemically stable stationary phase possessing mechanical strength in a particle size able to flow reasonably easily for column packing.

1.3 Polymerization Processes:

There are two principal types of polymerization processes for polymer formation.

(A) Condensation polymerization/Polymer

Condensation polymerization in which the monomers interact by an ionic reaction mechanism, involving the elimination of small molecules such as water, alcohol or ammonia and forming new C - C, C - N, C - O or other bonds. The structure of the monomer being such that the process can repeat itself in building up on the polymer molecule. Since molecules are lost, the ultimate analysis of the polymer is different from that of the monomer from which it was formed (I-S-1).

(B) Addition polymerization/Polymer

Addition polymerization in which the monomers interact by the free radical mechanism without forming any other products and the polymer chains contain only C - C bonds. These are polymers in which the molecular formula of the repeating unit is identical with that of the monomer, and the molecular weight of the polymer is a simple summation of the molecular weights of all combined monomers units in the chain (I-S-2).

1.4 Ion-exchange materials:

Ion-exchange materials are of wide variety. These may be organic or inorganic, natural or synthetic. Synthetic materials are usually superior because their properties can be better controlled. The most important class of ion-exchangers are the organic ion-exchange resins. They are typical gels, their framework, the so called matrix, consists of irregular, macromolecular, three dimensional network of hydrocarbon chains. Depending on the acidity or basicity of functional group attached to the matrix, the ion-exchange resins are classified as cation exchange resins (weakly or strongly acidic) and anion exchange resins (weakly or strongly basic).

Cation-exchange resins:

An ion exchange resin capable of exclusively exchanging cation is classified as a cation exchanger.

The early cation exchangers were naturally occuring zeolites, but these have been almost completely superseded by the synthetic ion-exchangers.

The first synthetic ion-exchangers were prepared in 1935 using a phenol-formaldehyde polymer for the cation exchanger.

The synthetic cation exchangers are classified into two main groups, the weak-acid cation exchangers with hydroxyl (-OH) and carboxylic acid (-COOH) groups (I-S-3) and the strong acid cation exchangers with sulfonic ($-SO_3H$) acid groups (I-S-4). The strong acid cation exchangers are made either by sulfonation of phenol - formaldehyde polymers, sulfonation of styrene - divinylbenzene polymers or by polymerization of phenolsulfonic acid with formaldehyde.

Recently, other cation exchangers with different properties and acid strengths have been developed. These resins carry phosphoric ($-PO_3^{2-}$), phosphonic ($-HPO_2^-$), arsenic ($-AsO_3^{-2}$) and selenonic acid ($-SeO_3^-$) groups.

Cation exchanger can also contain two different functional groups with the same charge, such as sulfonic acid and carboxyl groups, such resins are called "bifunctional" or "polyfunctional".

Reaction Mechanism of Cation Exchange Resins:

The reaction of phenol with formaldehyde in the absence of some suitable catalyst is relatively slow. The nature of the reaction product depends considerably upon whether an acidic or basic catalyst is used. The mechanism of the addition of formaldehyde to a phenol is still not clearly understood. However, the phenolic hydroxyl group activates the benzene ring so that a methylol ($-CH_2OH$) group always enters the nucleus in ortho and para position to the hydroxyl group. When one or more of the ortho and para positions are already occupied, the reaction becomes slower and when no position is available the reaction stops.

When alkaline catalysts are used, the primary reaction products are phenol alcohols, which are called "Resoles". In the presence of acidic catalyst, the primary reaction products are also phenol alcohols, but they rearrange rapidly to yield diphenylmethane derivative, to which the name "Novolacs" has been given (I-S-5).

A three stage mechanism for the condensation in alkaline catalyst have been proposed.

(i) Resol formation : This represents the initial condensation product of a phenol and formaldehyde giving mainly a phenol alcohol.

(ii) Resitol formation : This is the second stage of condensation wherein the molecular weight is increased to such an extent that the product is no longer soluble in alkalis. The product is partially or completely soluble in oxygenated organic solvents. Cross-linking has just started at this stage and the resin is still soft and plastic while hot, although hard and brittle when cold.

(iii) Resite formation : In this final stage of polymerization, a large amount of cross-linking has occured and the resin is completely insoluble and infusible and there is formation of methylene ($-CH_2-$) bridge.

In fact, the ionic character of the group is the same in the resin phase as it is in a simple organic compound. Thus all sulfonic acid exchange resins are strongly acidic in comparison to carboxylic acid resins, just as phenolsulfonic acid is strong in comparison to salicylic acid.

The ion-exchange behaviour of the resins is chiefly determined by the fixed ionic groups. The number of groups determines the ion-exchange capacity. The capacities of the weakly acidic exchangers are functions of the pH and the titration curves, i.e. curves of exchange capacity against pH have the form shown in (I-F-1). On the other hand, the capacities of the strongly acidic exchangers are substantially independent of pH, the capacity falling only at the extreme ends of the pH scale as shown in (I-F-2). The highest point on the titration curve represents the total capacity of the exchanger.

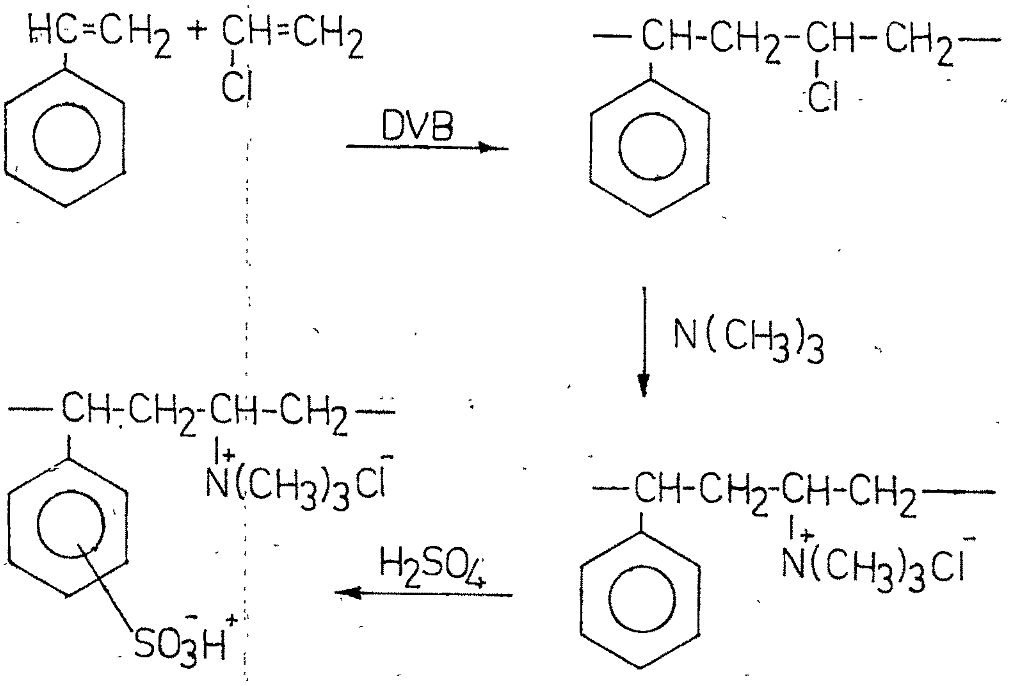
1.5 Amphoteric ion exchangers:

Amphoteric ion exchangers are those which contain both acidic and basic groups.

Condensation products of amines and phenols contain phenolic-OH groups of very low acid strength in addition to the primary, secondary, and tertiary amino groups. Specific cation exchangers, the resins with iminodiacetic acid groups, contain weak base groups in addition to carboxylic acid groups.

Amphoteric resins with strong-acid groups have been prepared (1, 2). More recently amphoteric resins with aminoalkyl-phosphoric and carboxylic acid groups have been synthesised (3, 4).

A resin with strong base and strong acid groups have been prepared (5), for example, by copolymerization of styrene, vinyl chloride, and a crosslinking agent, followed by quaternization and sulfonation of the product.



The most important class of amphoteric resins are the so-called "snake-cage polyelectrolytes". A snake-cage polyelectrolytes can be obtained by converting a strong-base anion exchanger to the acrylate form and then polymerizing the acrylate anions in the resin. The linear chains of the poly-counter ions are so intricately intertwined with the crosslinked matrix that they cannot be displaced by other counter ions; they are trapped like snakes in a cage. In a snake cage polyelectrolytes, the ionic groups of the poly-counter ioms are not linked to the matrix. Hence the charges of the poly-counter ions and of the matrix have more liberty to move relative to one another, and so they can neutralise one another. As a consequence, it is not essential for the resin to have a mobile counter ions to remain electrically neutral, provided that the charges of the fixed ionic groups and poly-counter ions are properly balanced. This type of resins are excellent reversible sorbents for electrolytes and are used for separations by "ion retardation".

1.6 Chelating Resins:

The conventional ion exchange resins separate ionic constituents by means of several mechanism or "bases of selectivity". First, they absorb ionic constituents in presence of nonionic substances. Second, anionic substances are taken up by the anion exchange resins, cationic substances by the cation exchange resins. Third, ions of higher valencies are preferentially absorbed in dilute solutions. Fourth, with resins of high degree of cross-linking, the ion having a smaller (hydrated) ionic volume is preferentially absorbed (6,7). Fifth, organic ions may be absorbed by the hydrocarbon matrix of resins (7,8). Sixth, an ion may interact chemically with a fixed exchange group and in that manner be taken up preferentially (9, 10, 11,12).

While a resin may thus take up one ion species preferentially over another, this selectivity usually occurs but to a limited extent and ion separations can be effected only by careful elution procedure in a column, where many hundreds of fractions can occur. The conventional ion exchange resins should then be classified as "selective" in that they are characteristic for a comparatively small number of ions (13).

A specific ion-exchange resin may correspondingly be defined as one that under proper experimental conditions is characteristic of one ionic species only. Chelating ion-exchange resins, in which chelate groups are substituents in a highly cross-linked and therefore insoluble hydrocarbon matrix. The use of organic chelate compounds is well known in analytical chemistry (14, 15). A chelate groups suitable for use in a resin must obviously have the following properties (a) be capable of resin formation or substitution in a resin matrix (b) be sufficiently stable to withstand the polymerization or resinification reaction and (c) be compact so as not to be hindered sterically by the dense resin matrix. An additional requirement is that both arms of the chelate structure be present on the same monomer in proper spatial configuration; thus a specific juxtaposition of both arms in the resin is required.

Natural Chelating Polymers:

Alginic acid is a polyuronide found in brown sea-weeds and its chemical formula is suggested as (I-S-6). The alginate in sea-weed behave as a base exchange material and is present as mixed salt of cations, mostly calcium, able to render it insoluble. The amount of divalent ions necessary to obtain precipitation of aliginates increases in the order Pb, Cu $<$ Ca $<$ Co, Ni, Zn, Mn (16). Through divalent ions, alginic acid may also be combined to other substances (17, 18). As alginate was found to be a very effective agent for inhibiting intestinal strontium uptake, it was proposed for prevention and therapy of strontium-radio contamination (19). Chromatography of metal ions and organic substances on aliginic acid has been studied by Cozzi and coworkers (20, 21, 22).

Chiten is a polysaccharide constituted of β-(1-4) 2-acetamido-2-deoxy-D-glucose units, some of them being deacetylated. It can be called poly-N-acetyl-D-glucosamine and be represented as (I-S-7).

It occurs widely in lower animals, fungi, etc. The exoskeletones of Crabs, lobsters, (arthropods) etc., are good sources of Chiten (23). Metal concentration factors in Zooplankton support Bowen's statement that among cations the order of affinity for living matter is tetravalent elements, trivalent elements, divalent transition elements, divalent group IIA elements, groups IA elements (24).

Chitosan is deacetylated chitin, and is conceived as a clarification aid and viscosity builder in solutions for rapid setting of suspended solids (25). It can also be obtained as a chelating membrane. Chitosan membranes generally show lower capacity than Chitosan powder (26). It is possible to use Chitosan, as a polymer for collection of trace metals by chelation accompanied by coprecipitation (27).

Many polysaccharide derivatives have been studied as natural chelating polymers (28). The polyanions are polyguluronate, polymannuronate, pectate, hyauronate, etc. Polysaccharides are present in soil humus (29) also. Ligand groups in soil organic matter may be found in arrays sterically favourable for the chelation of particular metal ions (30, 31).

Metal-coordination - complex formation in cartilage, elastin, etc. is important in primary calcification process (32). Wool is a complex protein containing hydroxyl, amino, amido, carboxyl, sulphydryl and disulphide groups. Wool protein has been investigated (33) for thin layer chromatography. Nucleic acids are also known to interact with various metal ions (34-37).

Synthetic chelating polymers:

Linear polymers

Linear polymers containing chelating sites can be obtained by addition polymerization or condensation polymerization.

Linear addition polymers containing chelating groups would have vinyl backbone. Styrene may be copolymerized with malic anhydride to produce (I-S-8). Polystyrene may be chloromethylated and then treated with

(i) imminodiacetate (IDA) to yield (I-S-9) or
(ii) a suitable chelating diamine to yield (I-S-10).

Dowex A-1 chelating resin has the polymer backbone structure of (I-S-9) and has metal chelating properties similar to IDA itself (38). Amino acid chelating resin structures have been prepared containing aminodipropionate, (39), glycine (40), anthranilic acid (41), pyridine dicarboxylic acid (42), hydroxamic acid (43) etc.

There has been considerable activity in the field of chelating ion-exchange polymers in recent years. Studies on ion-exchangers and organic/inorganic ligands lead scientists to develope ion-exchange polymers possessing chelating properties. In analytical as well as in preparative inorganic chemistry, there exists considerable need for chelating polymers which combine the ease of operation of the conventional ion-exchangers and specificity/selectivity of the ligands. The research schools which contributed considerably towards the preparation and understanding of the nature and behaviour of such chelating polymers are those of Bayer (44), Blasius (45), Gregor (46), Hering (47), Kennedy (48), Manecke (49), Schmuckler (50), De Geiso (51) etc. Such polymers can find use in column chromatography, thin layer chromatography, ligand exchange chromatography, membrane formation, desalination, waste water treatment etc.

Ion exchangers may be specific in terms of functional groups introduced in them through specific ligands. Because of its specificity, an ion exchanger can sorb (exchange) one ionic species to the exclusion of others under broad range of conditions. This is examplified below:

Skogseid (52) subjected polystyrene to nitration, reduction, condensation with picryl chloride and further nitration and obtained an ion exchanger having structure (I-S-11).

Dipicrylamine (I-S-12) is a specific precipitating agent for potassium.

Many compounds which form chelates with metal cations have been incorporated into resin structure by polycondensation with phenols and aldehydes. Examples are anthranilic acid (53, 54) (I-S-13) (specific for zinc and other transition metal ions), o-aminophenol (53, 55) (I-S-14), anthranilic acid diacetic acid (56) (I-S-15), m-phenylene diglycine (53) (I-S-16) and m-phenylenediaminetetracetic acid (56) (I-S-17).

When chelating agents are introduced into styrene type resins, ion exchangers are mechanically and chemically more stable than the condensation polymers. Various methods of preparing resins with iminodiacetic acid group are developed (57). In their complexing tendency these resins are similar to ethylenediaminetetraacetic acid (EDTA) (I-S-18). Hydroxamic acid groups have been introduced into a resin with carboxylic acid groups (58, 59), these resins are specific for Fe^{+3} ions. Resins with mercapto groups prefer Hg^{+2} ions (60, 61). Mercapto groups have also been introduced into polyamide resin such as nylon (60).

A resin with chromatropic acid groups preferring Ti^{+4} has been made (62). Agents such as β-naphthol have been introduced by coupling with diazotized resins (63, 64). Resins containing chlorophyll and haemin derivatives form extremely strong chelates with ions such as Fe^{+3} (65, 66)

Gregor, Taifor and Backer (67) investigated various ion exchangers exhibiting chelating properties towards the transition elements. The most promising resin found by these investigators was prepared from m-phenylenediglycine, o-aminophenol and formaldehyde. When compared with ordinary carboxylic or amine resin, these resins showed selectivities for transition elements that could not be accounted for by simple ion exchange processes.

A resin containing a beta diketone group and exhibiting a very high selectivity for copper has been synthesized by Mc Burney (68).

Kennedy and co-workers (48) found that polymerized and insolubilized phosphonates (I-S-19) were selective for uranyl, ferric, cobalt and lithium salts in non-aqueous solvents such as ketones and primary alcohols. These polymeric adsorbents exhibit little or no ion exchange capacity in the usual sense, however the iron, uranyl, cobalt and lithium salts are adsorbed by these resins as Werner coordination complexes and these may be eluted with acetone-water solution or dimethylformamide.

Phenolics would be formed by the polycondensation of phenol derivative with formaldehyde (69) and aminoplasts by the polycondensation of amide derivative with formaldehyde (70). Phenolics resins have been used as cation exchange resins. In recent years, attempts have been made to obtain resins by the polycondensation of phenol derivative (chelating agent) with formaldehyde. Salicylic acid-formaldehyde condensation resins have been reported by Topp (71), De Geiso et al (72), Komiya et al (73) Rabeck et al (74), Davies et al (75). A chelating resin based on anthranilic acid-resorcinol - formaldehyde has been reported by Gregor (53) and Von Lillin (76). Hojo et al (77) reported a chelating resin based on gallic acid-phenol-formaldehyde. A chelating resin based on 8-hydroxyquinoline - resorcinol - formaldehyde has been reported by Von Lillin (76) and Parrish (64). A chelating resin based on o-aminophenol - formaldehyde has been reported by Gregor et al (53) and Pennington (55). Pennington et al (55) reported chelating resins based on resorcinol - formaldehyde, β-resorcylic acid - formaldehyde, resacetophenone - formaldehyde and o-aminophenol-formaldehyde. Resins from naphthoquinone/ anthraquinone derivatives and formaldehyde have been studied by Soloway (78), Maneck (79), Izoret (80) etc.

A series of specific, chelate forming ion exchangers has been prepared and studied mainly in the field of analysis.

A polymer with 8-hydroxyquinoline functionality, previously described, has been used for several metal separations and is specially selective for vanadium (81). Starting with macroporous crosslinked polystyrene, amide groups (82, 83), arsonic acid (84), dithiocarbamate (85), thioglycolate (86), Oxime (87, 88) and nitro-resorcinol units (88) have been attached, the products have the selectivities expected from those of the parent substances in solution. Oxime and thioglycolate resins, for example, are selective for mercury and copper; nitroresorcinol is selective for iron (III), copper and cobalt. A cellulose-based exchanger carrying salicylic acid absorbs iron (III) and uranium (VI), and one with hydroxyphenylazo-2-naphthol units absorbs uranium (VI) very strongly (89).

Instead of being chemically grafted to polymers, complex organic molecules can be held as strongly absorbed counter ions in ion-exchange resins, a mercaptoazobenzene-sulfonate, held in an anion-exchange resins, absorbs mercury (II) (90), an anion-exchanger loaded with substituted 8-hydroxyquinoline sulfonate absorbs many metal ions (91). The chelating agent may also be placed in the mobile phase, using a nonionic reverse phase support, which essentially becomes a cation exchanger (92).

Aim and object of the present work:

Seldom does one encounter a phenomenon that finds many applications in such widely divergent fields such as agriculture, biology, medicine and chemistry. In recent years, ion exchange has shown itself to be in such a position. Thus, ion exchange is firmly established as a unit operation and is an extremely valuable supplement to other procedures such as filtration, distillation and adsorption. All over the world, numerous plants are in operation, accomplishing tasks that range from the recovery of metals from industrial wastes to the separation of rare earths and from catalysis of organic reactions to decontamination of water in cooling system of nuclear reactors. In the laboratory also, the ion exchangers are used as an aid in analytical and preparative chemistry. Even a perennial challenge of purification and demineralization of water has been fulfilled by the ion exchangers.

Thus, the recent appearance of high-capacity and durable ion exchange resins has stimulated much interest in ion exchange with the result that the number of applications involving ion exchange resins has "mushroomed" fantastically.

The most important ion exchange are the synthetic resins which are superior to the other materials in their chemical and mechanical stability, ion-exchange capacity, ion exchange rate and versatility. Much more research has been done in the field of synthesis and applications of cation as well as anion exchange resins but comparatively meagre research has been carried out regarding the synthesis of new chelating amphoteric ion exchange resins and their applications in various fields. Thus, the recent evergrowing vista of applicability of ION-EXCHANGE RESINS in various fields has given inspiration to so many investigators to rush for finding new ION-EXCHANGE RESINS.

Further, a great deal of effort has been directed towards the synthesis of chelating or complexing resin structures (93, 94, 95, 96) and ion selective resins, amphoteric ion exchange resins, inter polymeric resins and pellicular resins, etc. for various reasons. Such polymers can find use in column chromatography, thin layer chromatography, ligand exchange chromatography, membrane formation, desalination, waste water treatment etc.

Literature survey illustrates that meagre work is reported on condensing agents other than formaldehyde and on condensation of naphthol acids, polyhydric phenols etc.

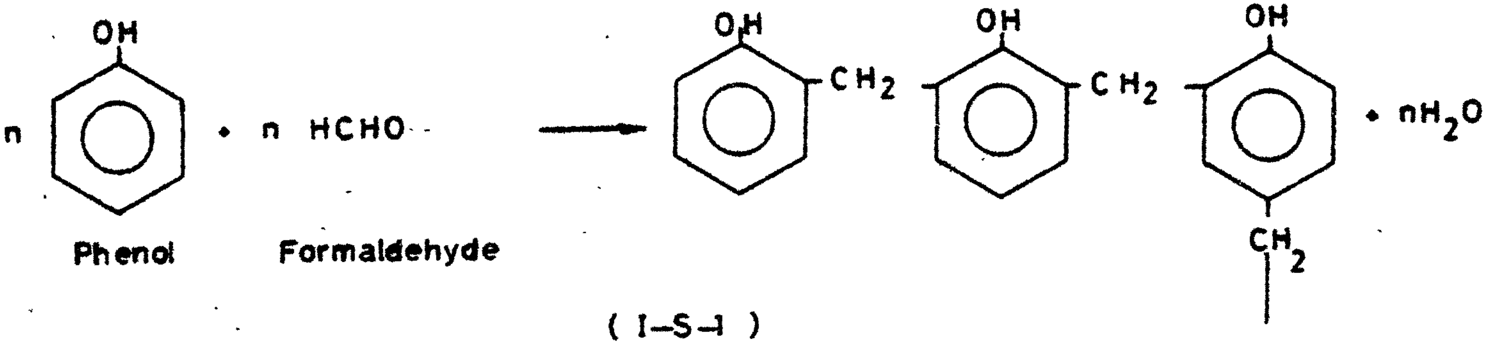
Hence we planned

(I) to synthesise (a) Phenol-Epichlorohydrin-Diethylenetriamine type, (b) Phenol-Epichlorohydrin - Triethylenetetramine type, (c) Phenol - Epichlorohydrin - Tetraethylenepentamine type chelating amphoteric ion exchangers and to evaluate them with respect to their pertinent and distinguishable properties such as moisture retention ability, true density, apparent density, void volume fraction, concentration of ionogenic groups, volume capacity, total ion exchange capacity, copper exchange capacity, rate of ion exchange, pH-titration studies, apparent pK_a and pK_b values, isoionic point values, thermal stability of the resins in various forms (such as H - , OH - , Na - and Cl - forms) at different temperature, the effect of temperature of equilibration on the capacity of the resins, oxidative degradation, swelling behaviour in various solvents and absorption specificity towards pre-transitional Ca(II) and Mg(II), transitional Co(II) and Ni(II) and post-transitional Cu(II) and Zn(II) metal cations in ammonium acetate-dimethylformamide media.

(II) to synthesise Phenol-Acetaldehyde-Thiourea type chelating amphoteric ion exchangers and to study their physico-chemical properties such as moisture content, true density, column density, void volume fraction, concentration of ionogenic groups, volume capacity, total ion exchange capacity, copper exchange capacity, rate of ion exchange, pH-titration curves, the apparent pK_a and pK_b values, isoionic point [redacted] values, thermal stability of resins in H - , OH - , Na - , K - and Cl - forms at various temperature, and oxidative degradation.

(III) to synthesise a phenol-Furfural - Hexamine type chelating amphoteric ion exchange resin and to characterise it by its characteristics viz., moisture content, true density, column density, void volume fraction, concentration of ionogenic groups, volume capacity, copper exchange capacity, rate of exchange, pH-titration curve, apparent pK_a and pK_b values, isoionic point value, thermal stability of H - , OH - , Li - , Na - , K - and Cl - forms at various temperature, oxidation resistance and absorption specificity towards Ca(II) and Mg(II) [pre-transitional], Co(II) and Ni(II) [transitional] and Cu(II) and Zn (II) [post-transitional] metal cations in ammonium acetate - dimethylformamide media.

Investigations carried out with the above considerations in view and the results obtained are discussed in the following pages.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OH
CH$_2$
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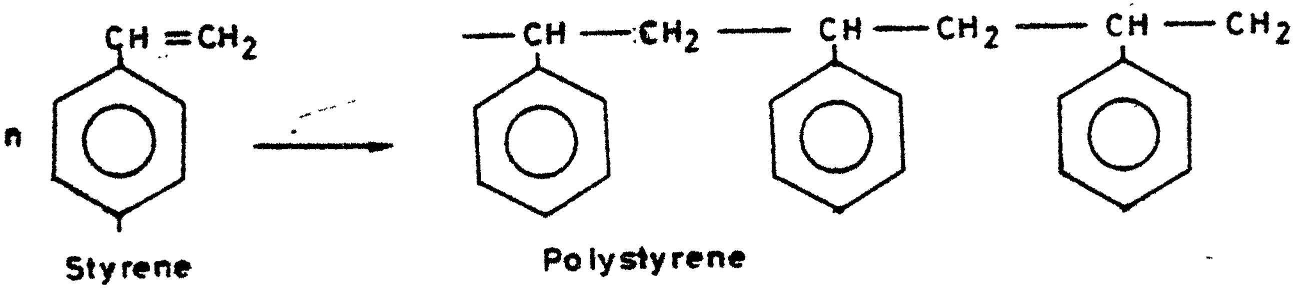
CH$_2$
+ nH$_2$O

(I–S–1)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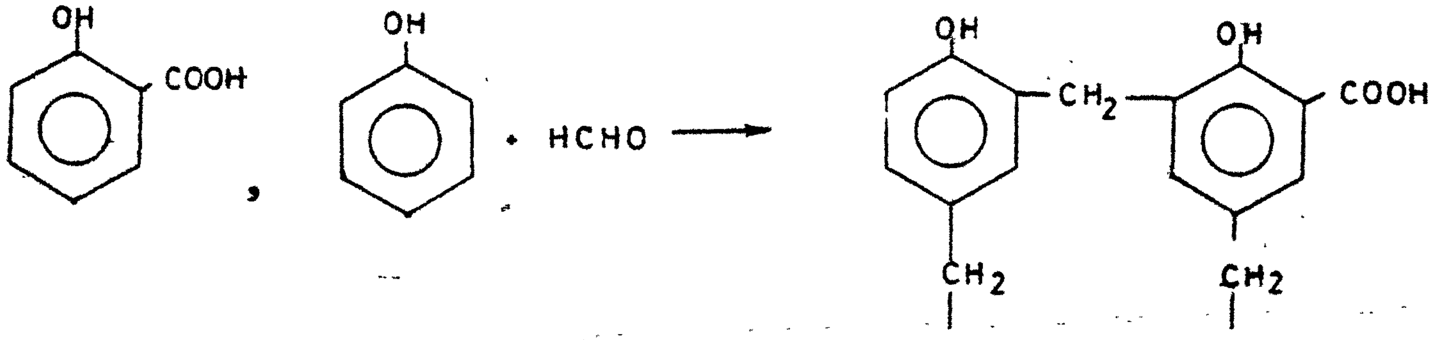
(I–S–2)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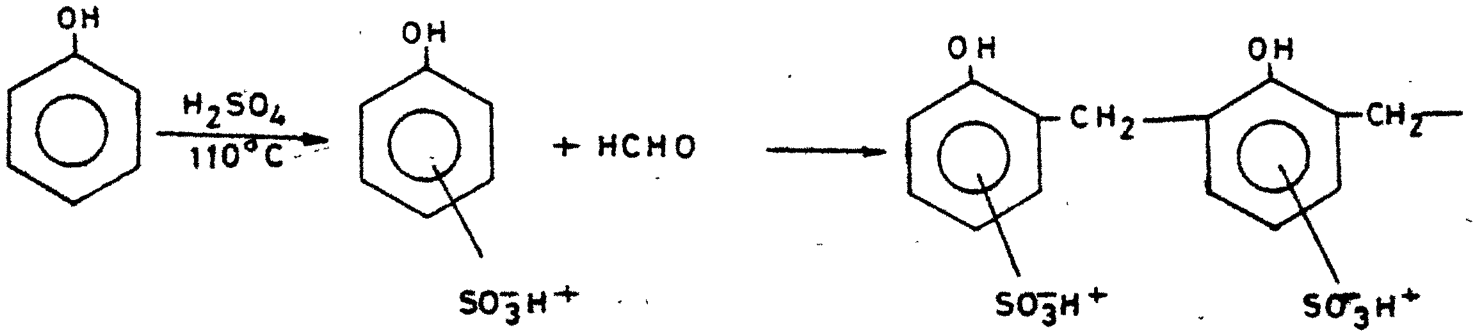
CH$_2$

(I–S–3)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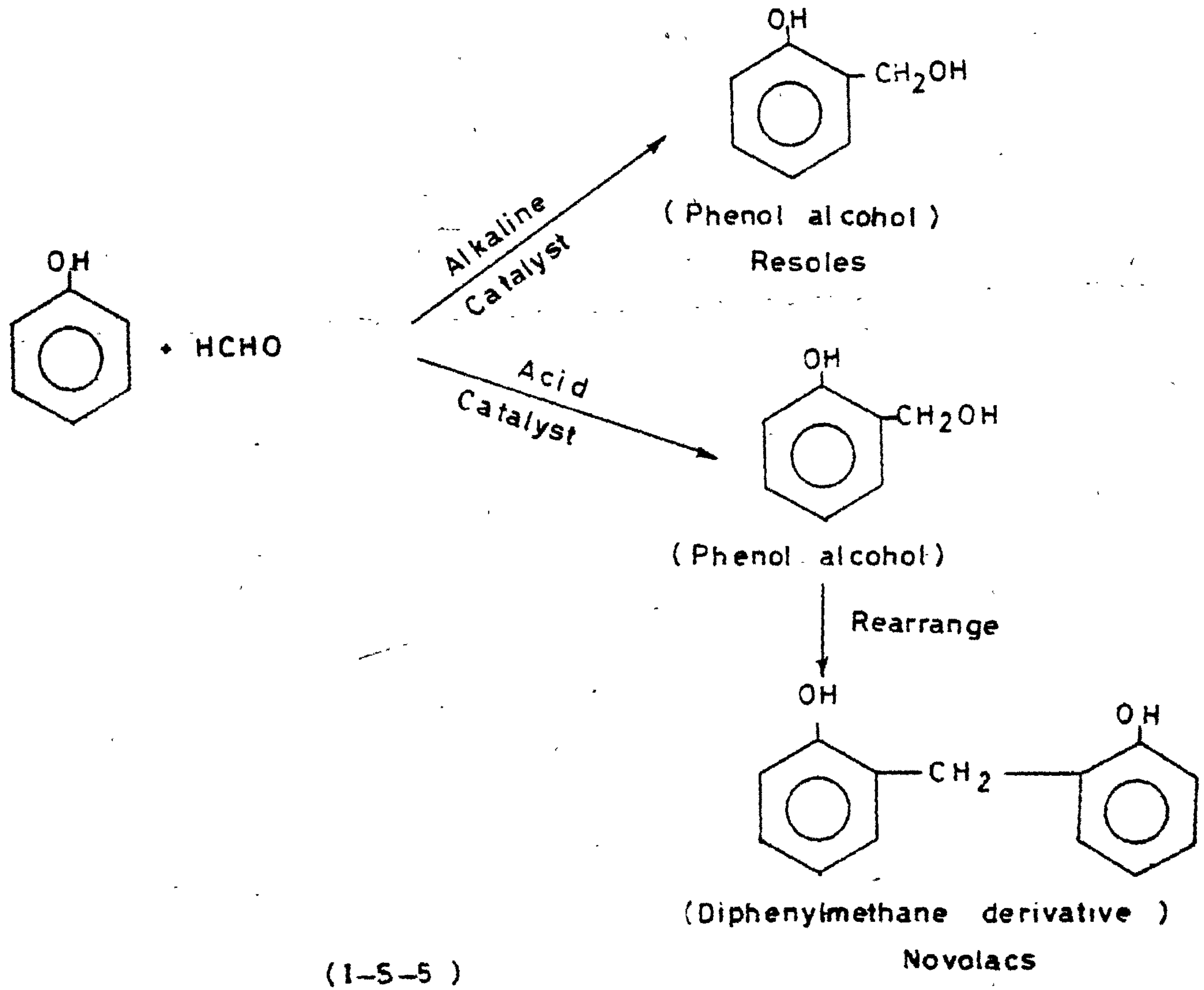
(I–S–4)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Alkaline
Catalyst
Acid
Catalyst
OH
CH2OH
(Phenol alcohol)
Resoles
OH
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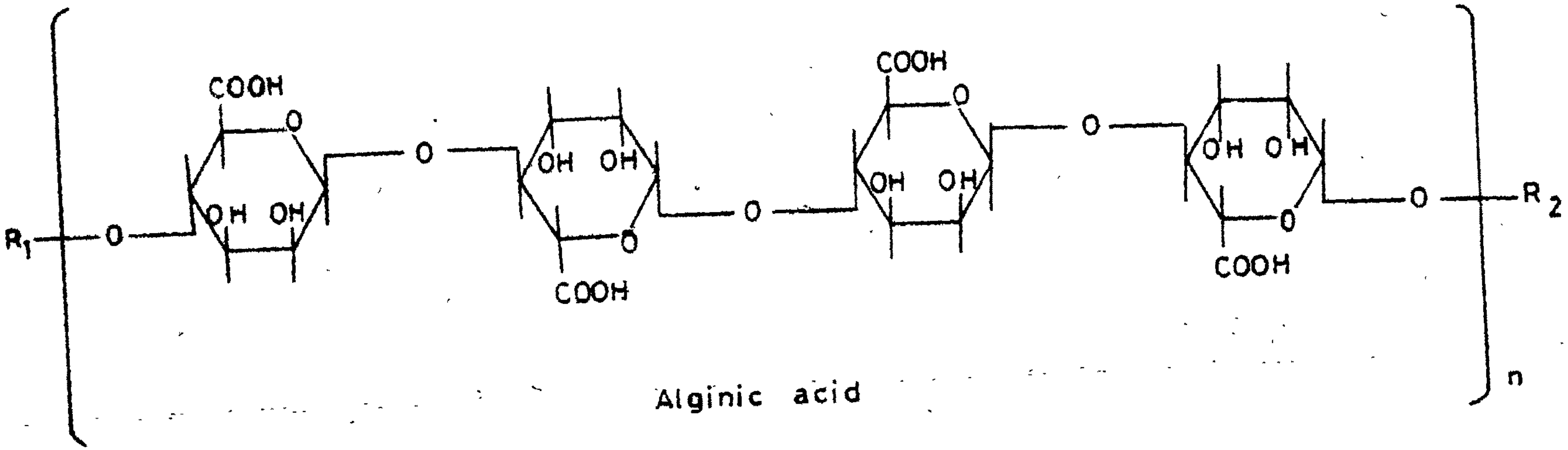
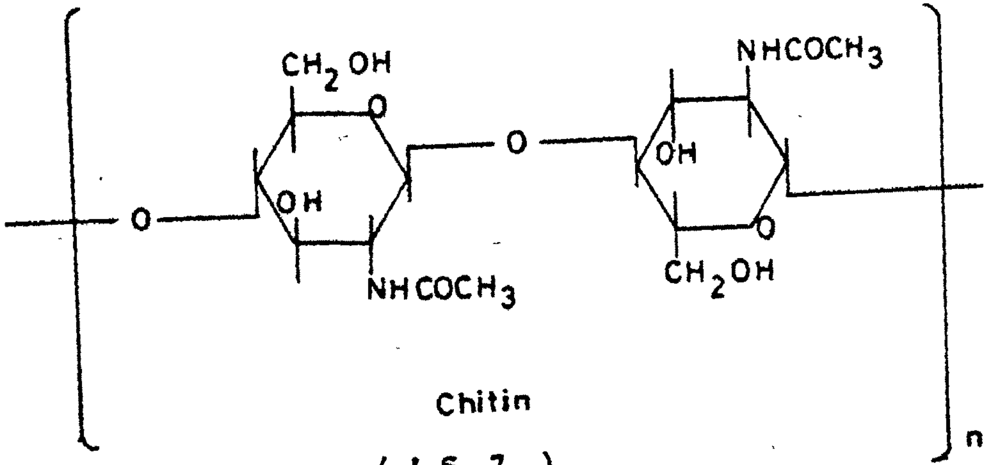
(Phenol alcohol)
Rearrange
OH
CH2
OH
(Diphenylmethane derivative)
Novolacs

(1–5–5)



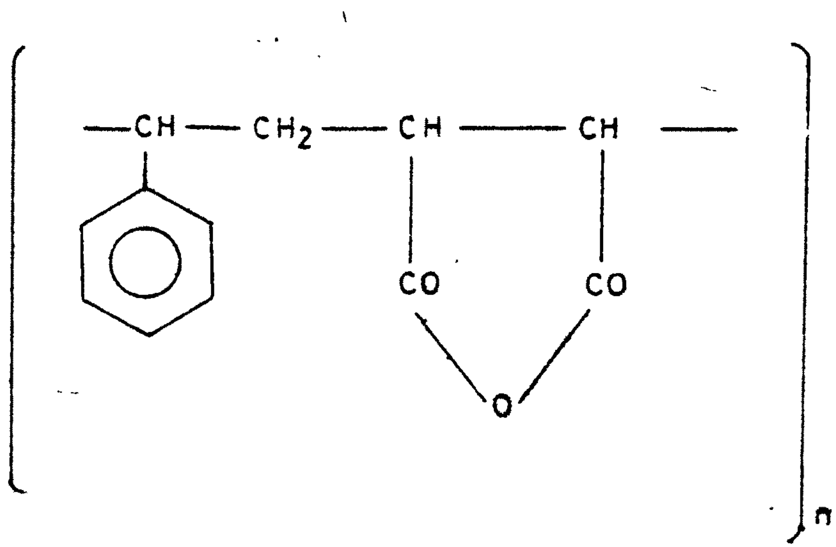
Alginic acid

(I–S–6)

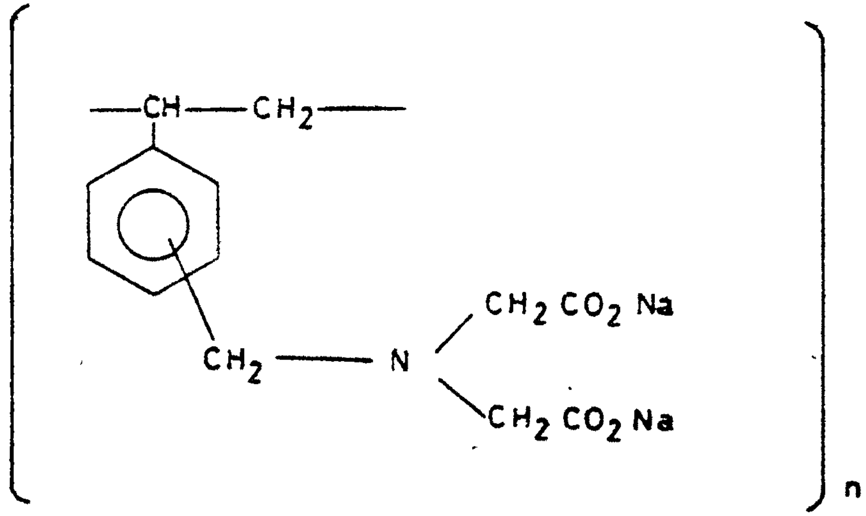


Chitin

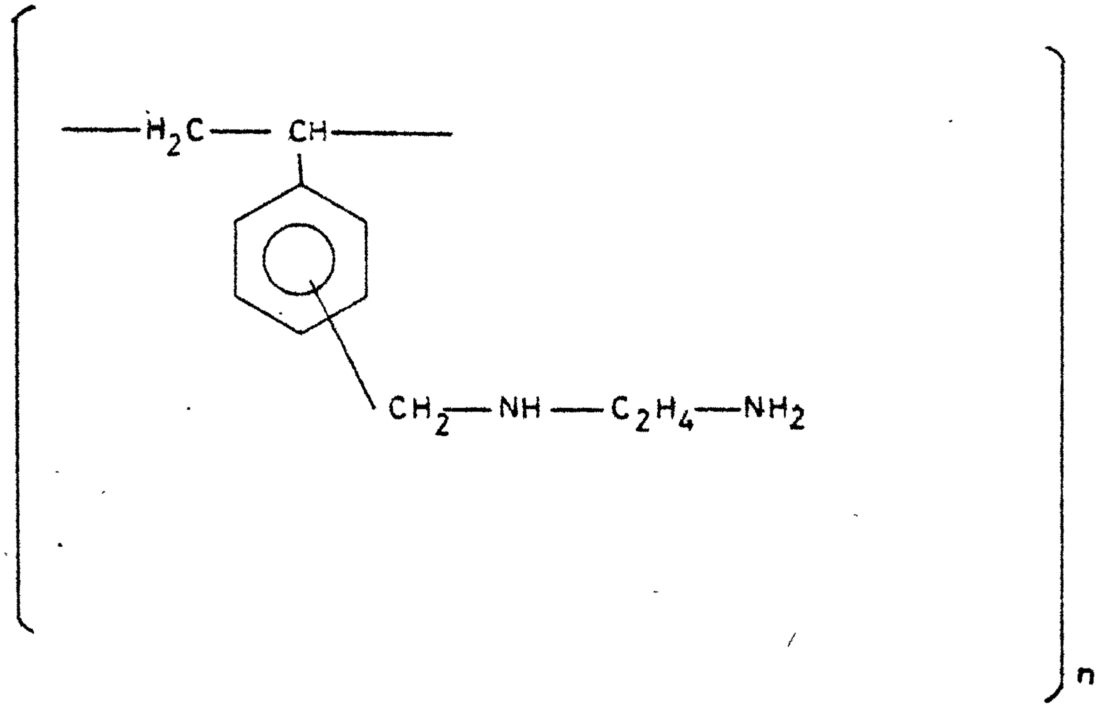
(I–S–7)



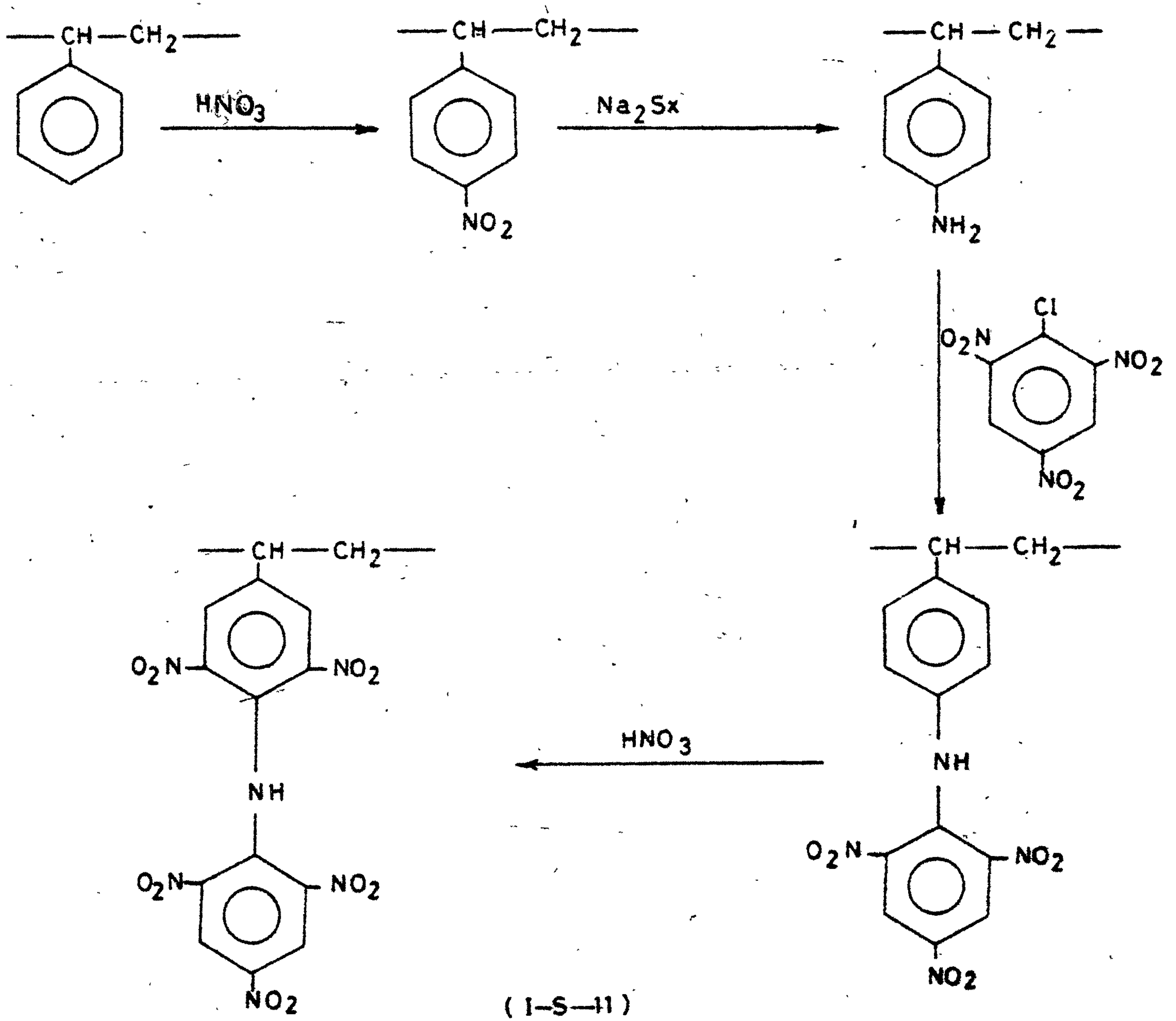
(I-S-8)



(I-S-9)



(I-S-10)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NH
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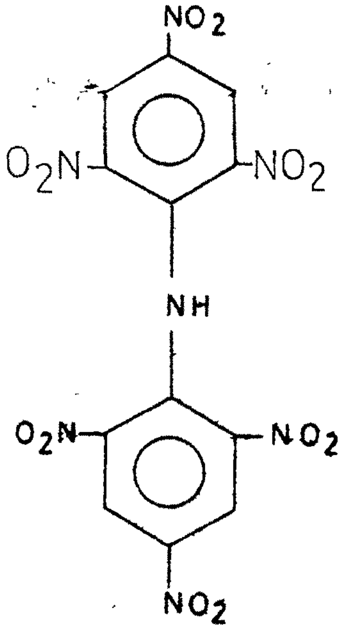
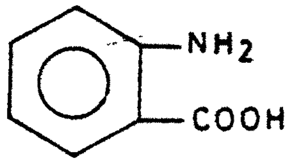
NO2
NO2

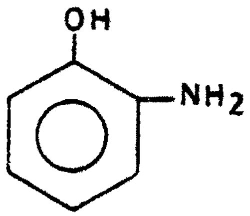
(I—S—II)



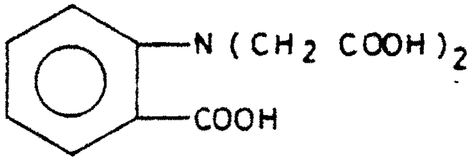
(I—S—12)



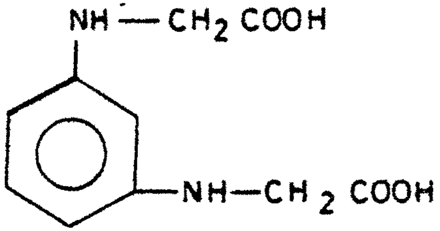
(I—S—13)



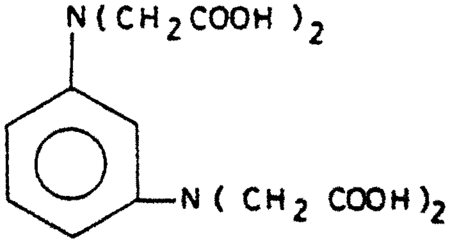
(I—S—14)



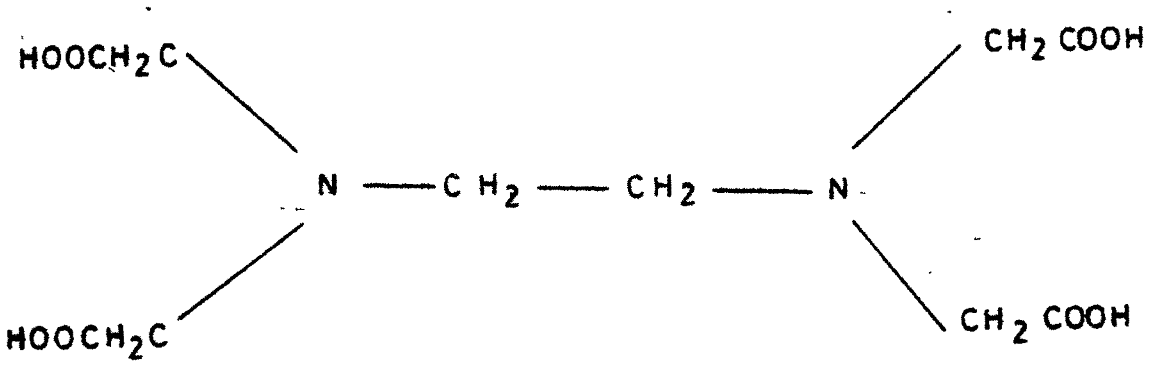
(I-S-15)



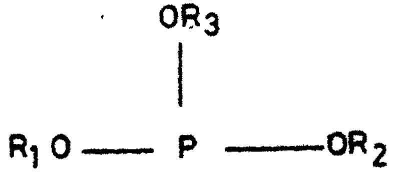
(I-S-16)



(I-S-17)



(I–S–18)



$$R_1O - \overset{\displaystyle OR_3 \atop |}{P} - OR_2$$

(I–S–19)

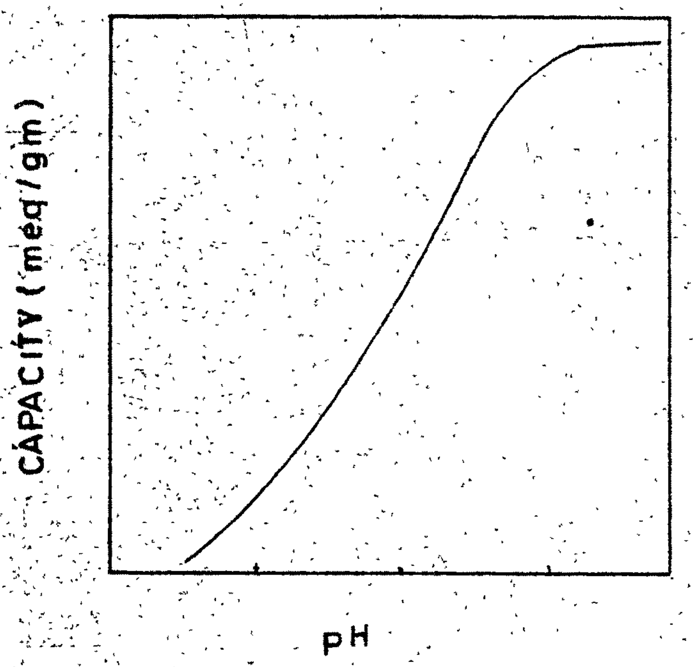


FIG.(I-F-1): TITRATION CURVE OF A TYPICAL UNIFUNCTIONAL WEAKLY ACIDIC RESIN

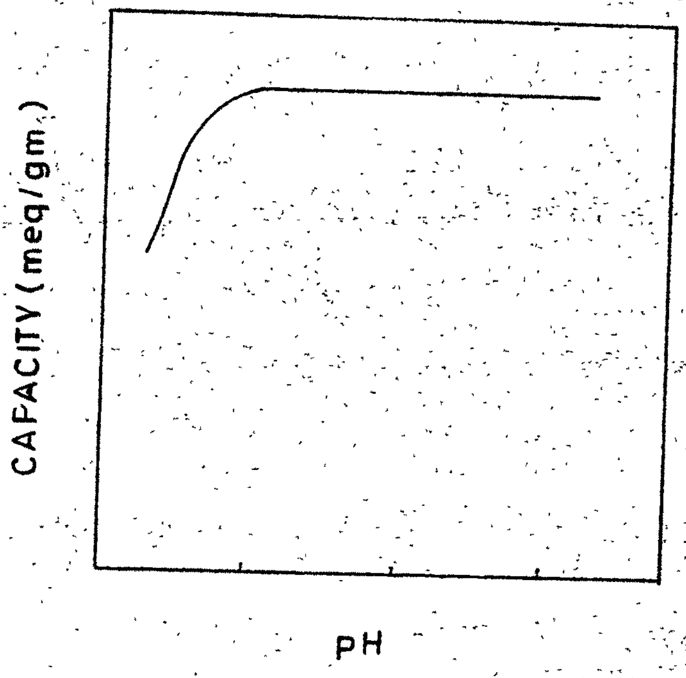


FIG.(I-F-2): TITRATION CURVE OF A TYPICAL UNIFUNCTIONAL STRONGLY ACIDIC RESIN.