ION EXCHANGE RESINS

By T. R. E. KRESSMAN, Ph.D., D.I.C., F.R.I.C.*

A lecture delivered before the Society on Friday, March 1st, 1957.

IN THIS account of ion exchange resins it is proposed to discuss the nature and properties of the resins and the principles underlying their action, and then to indicate how these properties can be applied to a few specific problems. This is a better approach than trying to present simply a catalogue of applications, because if the principles of the resins are known it is comparatively easy to see how they can be applied to one's own particular problems.

An ion exchange resin can be defined as an insoluble organic polymer containing labile ions that will reversibly exchange with other ions in a surrounding solution.

The resins were discovered by Adams and Holmes in 1935.[1] The first of these contained phenolic OH groups leading to cation exchangers, and aromatic amino groups leading to anion exchangers. The exchange of ions took place through these groups thus

$$R.OH + NaCl \rightleftharpoons R.ONa + HCl$$
$$R.NH_2 + HCl \rightleftharpoons R.NH_3Cl$$
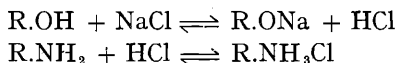
The capacities of these materials were low for two reasons :

1. The concentration of exchange groups in the resins was not very high (obviously a high capacity will result from a high concentration of groups).

2. The resins behave as weak acids and bases so that the equilibria lie rather to the left. Even when they were used in the form of columns and the reaction product—the HCl, say—was removed as fast as it was formed, the unfavourable equilibrium still resulted in a low working capacity.

Development of the resins, therefore, followed the lines of increasing the strength of the exchange groups and of increasing the number of the groups per unit weight of resin. Increasing the strength was a comparatively simple matter and cation resins, for example, were quickly developed that contained SO_3H groups, while anion exchange resins containing aliphatic amino groups followed shortly afterwards. Later, resins containing rather less strongly acidic groups in the form of COOH groups were developed and still later anion exchange resins containing strongly basic groups—quaternary ammonium groups—appeared.

Thus each type of exchanger—cation and anion—now has its counterpart of weakly and strongly ionised groups, and their properties can be illustrated by their titration curves (see Figs. 1–4). It should be noted that

* The Permutit Company Limited, Chiswick, W.4.

Purchased for the exclusive use of nofirst nolast (unknown)
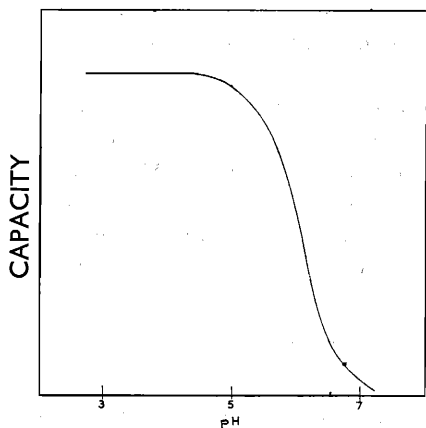From: SCC Media Library & Resource Center (library.scconline.org)

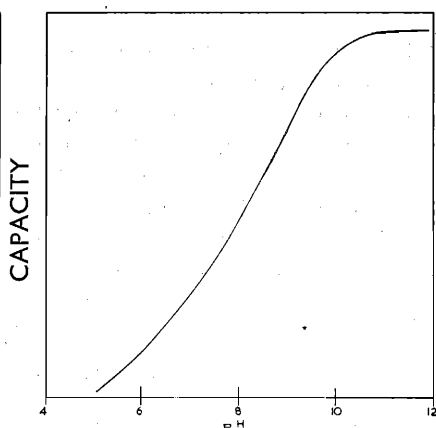Fig. 1. Titration curve of weakly basic resin.

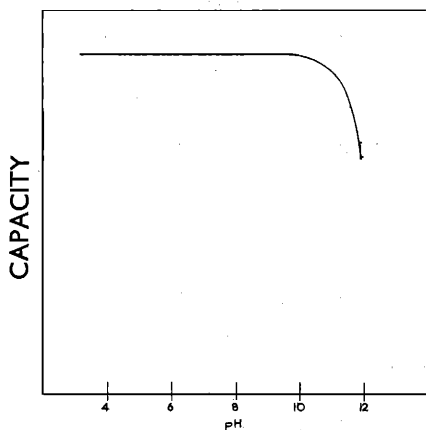Fig. 2. Titration curve of weakly acidic resin.

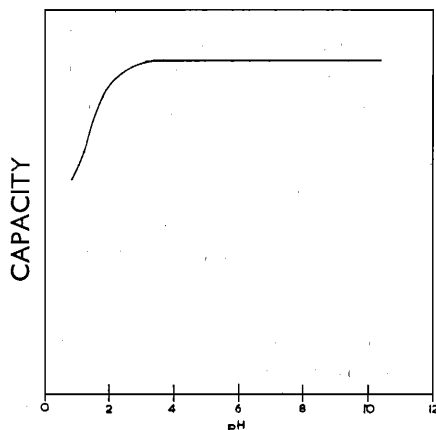Fig. 3. Titration curve of strongly basic resin.

Fig. 4. Titration curve of strongly acidic resin.

these are roughly mirror images in pairs, and the two anion exchange resins behave on the one side of neutrality exactly as the two cation resins behave on the other side.

The sulphonic resins are used where it is required to exchange all cations in solution for, say, hydrogen ions because the reaction

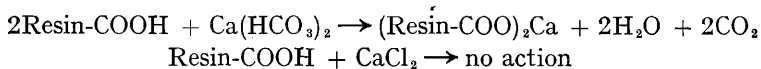$$R.SO_3H + NaCl \rightleftharpoons R.SO_3Na + HCl$$
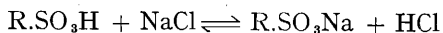
goes sufficiently far to the right that if we work in a column so that the HCl is removed as fast as it is formed, complete exchange will occur and the reaction can be written in effect

$$R.SO_3H + NaCl \rightarrow R.SO_3Na + HCl$$
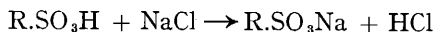
These resins are also used for ordinary neutral exchange, *e.g.*, sodium for calcium or potassium.

The weakly acidic resins—the carboxylic resins—show a very low capacity towards neutral salts but their hydrogen ions can be exchanged for the cations of salts of weak acids as, for example, bicarbonates. This is useful in the treatment of water for cooling systems where it is required to remove the scale-forming hardness (bicarbonates of calcium and magnesium), but where the permanent hardness (chlorides and sulphates of calcium and magnesium) is not particularly undesirable :

$$2\text{Resin-COOH} + \text{Ca(HCO}_3)_2 \longrightarrow (\text{Resin-COO})_2\text{Ca} + 2\text{H}_2\text{O} + 2\text{CO}_2$$
$$\text{Resin-COOH} + \text{CaCl}_2 \longrightarrow \text{no action}$$

Weakly basic anion exchange resins will take up strong acids like the mineral acids and, to a lesser extent, weak organic acids like acetic acid. They have no capacity in alkaline solution. The strongly basic resins, on the other hand, will take up not only strong acids and the ordinary weak acids to a high capacity, but such feeble acids as H_2S, boric acid, CO_2, silica and phenols. They will also exchange anions in neutral solution just as the strongly acidic cation resins will exchange cations in neutral solution :

$$\text{Resin.Cl.}^- + \text{NaNO}_3 \rightleftharpoons \text{Resin.NO}_3^- + \text{NaCl}$$
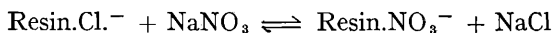
and will exchange OH^- ions just as the sulphonic resins will exchange H^+ ions :

$$\text{Resin.OH} + \text{NaNO}_3 \rightleftharpoons \text{Resin.NO}_3 + \text{NaOH}$$

The earlier resins were prepared by condensing formaldehyde with a phenol[2] or a phenol sulphonic acid[3] to yield cation exchangers, and with an amine[4] to yield an anion exchanger. Generally the condensation was performed with a compound containing the active exchange groups that the final resin was desired to carry. More recently, however, resins have been prepared by polymerising unsaturated compounds like styrene and then attaching the appropriate groups to the polymer by suitable chemical treatment. All four types have been prepared in this way. The nature of these polymers is such that, in general, a larger number of active groups can be introduced into them per unit weight than into the older type of condensation polymers. This means that the newer types have higher capacities than the old and in addition they are more stable.
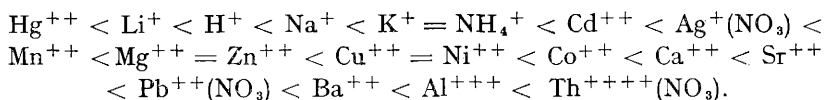
Since the ion exchange groups (NH_2, NR_4, SO_3H, $COOH$) are hydrophilic groups, the tendency is for them to pass into solution when the resin is brought into contact with water. As the groups are attached to the polymeric resin structure, they tend to draw the whole resin into solution also. To prevent this, the polymer structure has to be tied together with cross links in order to form a three-dimensional molecule. These cross links restrain the tendency of the resin to dissolve and the result is that the ion exchange

resin merely swells when the dry substance is placed in water. If the degree of cross linking is too low a further change in volume will occur during the exchange of one ion for another ; if the cross linking is too high the exchange of ions becomes undesirably slow. In practice sufficient cross linking is used to strike a balance between these two opposing effects.
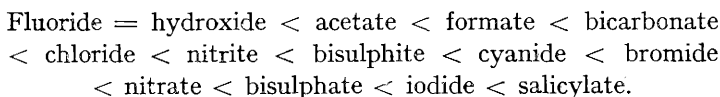
Ion exchange in resins is not merely a surface phenomenon and the whole of the particles is available for exchange, the exchanging ions being able to travel to the centres of the particles in a comparatively short time. The ions reach the centre by moving along the water-filled pores of the resin and these pores are of molecular dimensions, generally between about 5 and 15 Å diameter according to the resin. Ions larger than this cannot pass down the pores and a limited exchange capacity is observed with such ions. In fact, this can be exploited to separate small ions from large ones.

The position of equilibrium is determined by the "affinities" for the resin of each of the two ions taking part in the exchange. For instance, in the exchange between H^+ on a strongly acidic resin with Na^+ in solution the equilibrium lies rather more than half-way to the right, indicating that the sodium ion has a slightly higher affinity for the resin than the hydrogen ion. By measuring the position of equilibrium reached with a resin in some standard ionic form—the hydrogen form, for example—and solutions containing a series of salts with other cations, a table of affinities can be constructed. Similarly, by taking an anion exchange resin in, say, the chloride form, and allowing it to come to equilibrium with a series of salts containing other anions, a table of affinities for anion exchange can be obtained.

The order of affinities of some cations from $0.1N$ chloride solution for a phenol sulphonate resin[5] is :

$$Hg^{++} < Li^+ < H^+ < Na^+ < K^+ = NH_4^+ < Cd^{++} < Ag^+(NO_3) <$$
$$Mn^{++} < Mg^{++} = Zn^{++} < Cu^{++} = Ni^{++} < Co^{++} < Ca^{++} < Sr^{++}$$
$$< Pb^{++}(NO_3) < Ba^{++} < Al^{+++} < Th^{++++}(NO_3).$$

The order of affinities of some anions for a quaternary ammonium anion exchange resin[6] is :

Fluoride = hydroxide < acetate < formate < bicarbonate
< chloride < nitrite < bisulphite < cyanide < bromide
< nitrate < bisulphate < iodide < salicylate.

As already mentioned, a weakly basic anion exchange resin in the free base form will not take up anions appreciably from neutral salts but only from free acids. The affinities under these circumstances will be largely determined by the strength of the acid (as measured by its dissociation constant) and its basicity, and the order of affinities of a few acids for a resin of this type is $HCl = HNO_3 < H_2SO_4 < H_3PO_4$, and benzoic < oxalic < formic < acetic = citric < salicylic. If the resin is converted to an

ionic foim other than the free base form, say the chloride form, the order of affinities is different[7] : fluoride < chloride < bromide = iodide = acetate < phosphate < nitrate < tartrate < citrate < chromate < sulphate < hydroxide.

APPLICATIONS

The applications of the materials can be broadly listed under three headings :

(1) Complete removal of ions from a solution : (a) undesirable ions from a valuable solution ; (b) valuable ions from an otherwise valueless solution.

(2) Separation and concentration of electrolytes.

(3) Substitution of specific ions in solution by other ions.

Removal of undesirable ions from a valuable solution can be achieved comparatively simply if the valuable substance is not itself taken up by the exchanger, as will be the case if it is non-ionic or it is present as a complex or if it is ionised but is too large to pass down the resin pores. For the complete removal of electrolytes from a solution the demineralisation technique, using first a hydrogen exchanger and then an anion exchanger to remove the acids so formed, would be used. Alternatively, the mixed bed technique can be used, in which the cation and anion exchangers are mixed together and the solution to be demineralised is flowed through a single column of the mixture. Examples are the removal of electrolytes from sugar solutions, from glycerine solutions and from solutions of other non-ionised organic substances. Mercuric chloride is largely unionised in solution and impurities can be removed by passing the solution through a hydrogen exchanger, which scarcely affects the mercury salt.

The mixed bed technique is also useful for removing all the salts present in tap water, and water conforming to the B.P. standard for distilled water can be obtained in this way. Indeed, in the latest edition of the Pharmacopœia the previous item "distilled water" has now been amended to "purified water," and this includes water produced from a mixed bed of ion exchange resins[8].

The removal of valuable ions from an otherwise valueless solution can be carried out by using the appropriate resin which is chosen such that the valuable ions are taken up by the resin and the impurities pass through. On regenerating or eluting the resin—the cation resin with acid and the anion resin with alkali—the valuable ions appear in the regenerant effluents in concentrated form and can be recovered, for example, by a suitable chemical method. An example of this is the recovery of streptomycin on a carboxylic resin. The mould that produces streptomycin is grown in a nutrient salt solution in the presence of air, and when it has finished its work it is filtered off from the solution, which now contains the streptomycin along with the inorganic nutrient salts. This solution is passed through a carboxylic resin

in the sodium form which takes up the streptomycin and allows everything else to pass through. The streptomycin is then eluted from the column with dilute HCl or dilute sulphuric acid to give streptomycin hydrochloride or sulphate respectively.

The separation of ions is carried out by taking advantage of the different affinities of the various ions for the resin. This technique is used a great deal in chemical analysis, mainly in the analysis of inorganic substances since these are more frequently ionised than organic substances. However, organic acids and bases can be separated by using the appropriate resin. This is the principle of ion exchange chromatography. Perhaps the single field in which the most work has been carried out is that of amino acids. Some extremely elegant separations of amino acid mixtures containing as many as 50 amino acids have been carried out by Moore and Stein[9] in the U.S.A. and by Partridge[10] in this country.

Generally a resin is used of finer particle size than that for ordinary simple ion exchange procedures where 16–50 mesh particles are normal, and although sometimes 100–200 mesh material is used, most commonly it is less than 200 mesh. This is essential because only by the use of such fine particles combined with low flow rates can the near-equilibrium conditions be attained that are so essential to the production of sharp boundaries.

Any of the techniques of frontal analysis, displacement development or elution can be used, just as in conventional chromatography on, say, alumina.

In frontal analysis the solution containing the ions to be separated is flowed continuously through the column of resin, the ions of higher affinity displacing those of lower after an initial period in which all the ions are taken up—see Fig. 5. Only the ion of lowest affinity A^+ is obtained pure, and in consequence the method is only used when one component (and that having the lowest affinity) is required pure. An example of its use is in the separation of a weak and a strong acid, e.g., acetic and hydrochloric, on a weakly basic resin.

In displacement development the mixture of ions to be separated is absorbed as a band at the top of the column. A displacing solution is then flowed through the column, this solution containing an exchanging ion that has a higher affinity for the resin than any component of the original mixture. The ions ultimately move down and out of the column in the order of their increasing affinities, that with the least affinity appearing first—see Fig. 6.

This is the method used by Partridge. Its advantages are that the separated ions can be obtained in high concentration, and loadings as high as 50 per cent of the total capacity of the column can be used (i.e. the band extends half-way down the column). It can, accordingly, be used as a preparative method.
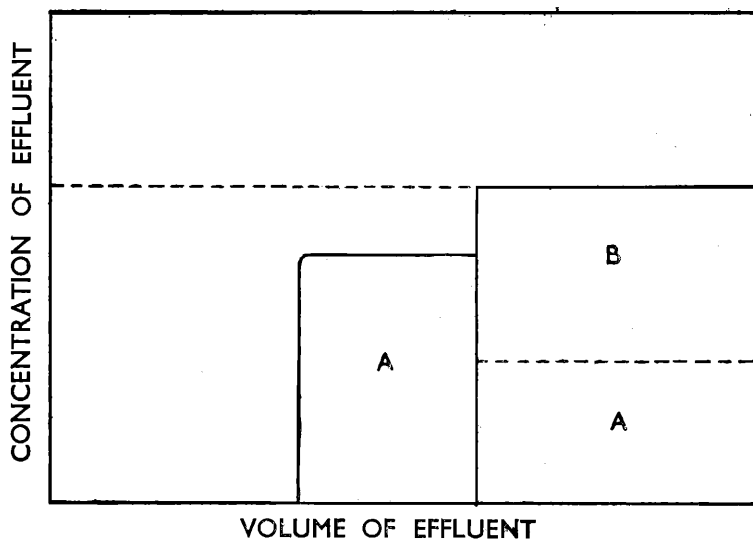
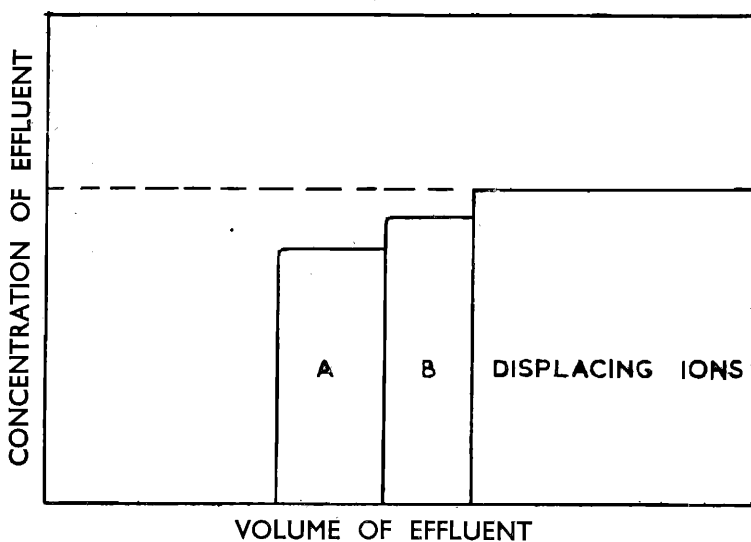Fig. 5.   Effluent composition in frontal analysis.

Fig. 6.   Effluent composition in displacement development.

Elution analysis is similar to displacement development except that the eluting solution contains an ion of relatively low affinity for the resin. The ions move out of the column and the elution curve resembles Fig. 7. The separated components are always contaminated with the exchanging ions of the eluting agent. For this reason an eluting agent is chosen such that it can be easily removed from the solution. Ammonia is frequently used, and so is formic acid, or ammonium formate. This method is the one used by Moore and Stein, and it is particularly useful for the separation of micro quantities of ions. It is not really suitable for preparative work since both the concentration and the loading are somewhat low.
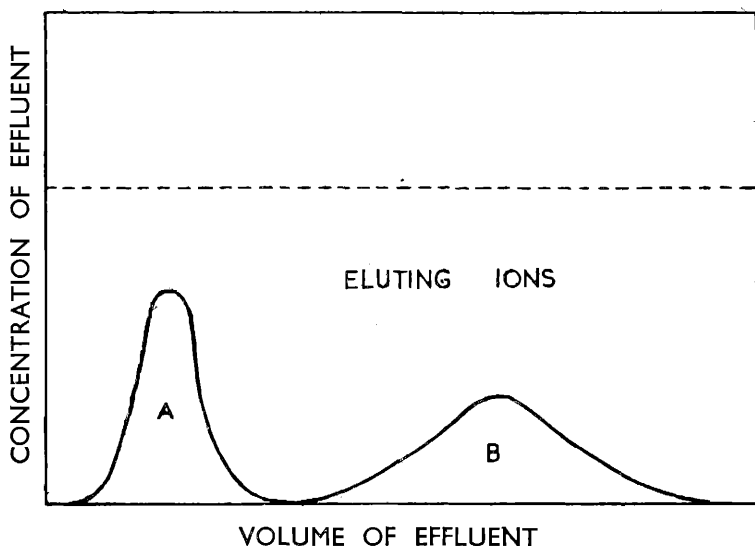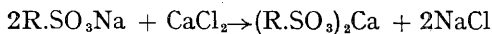

Fig. 7. Effluent composition in elution analysis.

The third heading—Substitution of Specific Ions in Solution by Other Ions—is generally simple and straightforward. The most common example is probably that of water softening, where calcium and magnesium ions are replaced in the solution by sodium ions

$$2R.SO_3Na + CaCl_2 \rightarrow (R.SO_3)_2Ca + 2NaCl$$

An important factor here is the relative affinity of the two ions in question. If the equilibrium lies strongly to one side, $i.e.$, the ion initially on the resin has a high affinity relative to that of the ion in solution, complete exchange will rarely occur. For instance, it is impossible to form a calcium salt by passing a dilute sodium salt solution over a calcium resin. (It is, however, possible to displace calcium by the use of a concentrated sodium salt solution
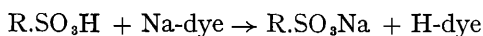
because in this circumstance the relative affinities of sodium and calcium are reversed and the sodium now has the higher affinity.) Likewise, it is impossible to form a solution of sodium phosphate by passing a dilute solution of sodium chloride over an anion exchange resin in the phosphate form.

This exchange of one ion for another is useful for preparing salts and acids that cannot be conveniently prepared by other methods. For a particular study, it was once required to prepare the tetra-ethyl-ammonium salt of Chlorazol Sky Blue. The quaternary ion was available as the bromide salt and the dye as the sodium salt. A solution of the quaternary bromide was passed through a strong base anion exchanger in the free base form
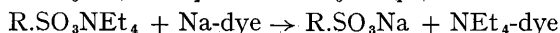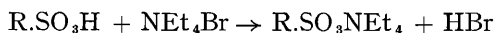
$$Resin.OH^- + Net_4Br \rightarrow Resin.Br^- + NEt_4OH$$
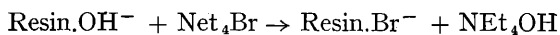
and the dye salt through a sulphonic resin

$$R.SO_3H + Na\text{-}dye \rightarrow R.SO_3Na + H\text{-}dye$$

and the free base and free acid solutions were then mixed until the pH was 7, as indicated by a pH meter.

The direct method

$$R.SO_3H + NEt_4Br \rightarrow R.SO_3NEt_4 + HBr$$
$$R.SO_3NEt_4 + Na\text{-}dye \rightarrow R.SO_3Na + NEt_4\text{-}dye$$

could not be used because the affinity of NEt_4^+ is so high compared with that of sodium that the last reaction does not, in fact, occur quantitatively.

A special case exists here when a solution of a free base is passed through a hydrogen resin, e.g.,

$$R.SO_3H + NaOH \rightarrow R.SO_3Na + H_2O$$
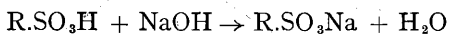
The effect is that the base has been completely removed from the solution. Similarly, acids can be removed with an anion exchange resin

$$R.NH_2 + HCl \rightarrow R.NH_3Cl$$
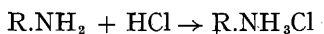
In addition to these more-or-less standard applications there are a few somewhat specialised applications. Mostly these depend on the simple replacement of one ion by another. For example, resins have been proposed as ingredients in antiperspirant and deodorant formulations. The resin will absorb fatty acids, ammonia and other products found in sweat, and they are mixed n a finely powdered form with a hydrophilic carrier substance. A typical formulation is 20 per cent carboxylic resin (in the form of particles —200 mesh) and 15 per cent aluminium phenol sulphonate dispersed in an oil-in-water emulsion.[11] Mixtures of cation and anion exchange resins have also been proposed for use in the same way, both as deodorants and to relieve dermatitis resulting from contact with plants like poison ivy.[12]

The resins have also been suggested as carriers for medicaments in ointments. For example, ointments comprising a carboxylic resin containing

adsorbed neomycin, and an anion exchanger containing sulphadiazine suspended in oil-in-water emulsions were claimed to show greater bactericidal action and more prolonged activity than those containing the free drugs.[13]

REFERENCES

[1] Adams and Holmes, *J. Soc. Chem. Ind.*, **54**, 1T (1935).

[2] Adams and Holmes, Brit. Pat. 450,308.

[3] Holmes and Holmes, Brit. Pat. 588,380.

[4] Adams and Holmes, Brit. Pat. 450,309 ; I. G. Farben A.G., Brit. Pat. 489,173.

[5] Kressman & Kitchener, *J. Chem. Soc.*, 1190–1208 (1949).

[6] Peterson, *Ann. N.Y. Acad. Sci.*, **57**, 144 (1953).

[7] Kunin and Myers, *J. Am. Chem. Soc.*, **69**, 2874 (1947).

[8] *British Pharmacopoeia* 1953, Addendum 1955, 73 ; *British Pharmaceutical Codex* 1954, Supplement 1957, 80.

[9] See, *e.g.*, Moore & Stein, *J. Biol. Chem.*, **211**, 893 (1954).

[10] See, *e.g.*, Partridge, Brimley and Pepper, *Biochem. J.*, **46**, 334 (1950).

[11] Rohm and Haas Co., U.S. Pat. 2,653,902.

[12] Rohm and Haas Co., U.S. Pat. 2,684,321.

[13] Fiedler, *Dissert. Abs.*, **15**, 1870 (1955).