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Base Exchange Properties Of Synthetic Resins

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have altered its physical and chemical properties so that its clayey residue behaves as a typical bleaching clay or Fullers Earth. Such clays are used for decolorizing of mineral, vegetable and animal oils and for fulling cloth. The naturally active clays are employed chiefly for bleaching edible oils. The bleaching action is thought to be due to the selective adsorption of coloring matter on the exposed particle surfaces which are in contact with the liquid to be decolorized. The adsorption is due to the presence of chemically open bonds or free valences on the surface. Good Fullers Earth is priced at from $10 to $15 per short ton. Many thousands of tons are available at or near the surface in Goodhue, Olmsted, Fillmore and Houston Counties.

BASE EXCHANGE PROPERTIES OF SYNTHETIC RESINS

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Baekeland in 1909 made available to us the first of the industrially important plastics. This was the condensation product of phenol and formaldehyde. It is interesting to note that despite the many types of resins which are now available, the first plastics developed, the phenol formaldehydes, are still today economically the most important.

Contrary to popular belief, the greatest tonnage goes into coatings of various types rather than into the molded and cast forms which are more easily identified by the public. The production of synthetic resins is still expanding rapidly as new uses are being found for them.

It was not until lately that attention was called to the fact that some of these resins possessed quite remarkable ion adsorption properties. This opens up an entirely new field of use for resins in the purification of water and the recovery of valuable metals from solution. The term base exchange is used in a reaction where metals replace each other. For example, a zeolite water softener operates by exchanging its sodium ions for the calcium and magnesium ions present in the water to be softened. These new resins are sometimes called "Organolites" because of the resemblance of their adsorptive properties to those of the inorganic zeolites. Besides their high capacities, one of the main advantages of these synthetic resins over the inorganic zeolites is their ability to withstand the action of dilute acids. Zeolites will gelatinize and break down in dilute acids whereas these resins as base exchange materials can repeatedly be regenerated with 2 or 5% hydrochloric, acetic, or sulfuric acids. This means that it is possible to recover heavy metal, such as copper, lead, bismuth, antimony, etc., which are difficult to recover from zeolites or these resins if sodium chloride instead of acid is used as the regenerating agent.

Among the most promising of these new base exchange resins are some which are very similar to the first resins prepared by Baekeland. For base exchange purposes, polyhydroxy benzenes rather than the simple phenol of Baekeland are condensed with formaldehyde to form insoluble cation exchanging resins. In our work we have been investigating the acid condensation product of formaldehyde and pyrogallol.

The method of preparation we have been using is quite simple. About two molecular proportions of formaldehyde are added to one mol of pyrogallol and the solution brought to the boiling point. On adding a few cc's of hydrochloric acid, a gelatinous reddish brown precipitate soon forms. This is washed with distilled water, broken up into pieces and dried in an oven near 100 ° C. The product is crushed and screened into fractions of the same size. These are placed in a tube and the absorption carried out by running the solution to be treated through a bed of the resins. After the resin is saturated, the metal is recovered by slowly running a relatively small volume of dilute acid through the bed.

A series of experiments on the method of preparation showed that even when excesses of either reagent were used, they reacted fairly closely in the ratio of 1.5 mols of formaldehyde to 1.0 mol of pyrogallol. This indicated a polymer structure with cross linkages which should be thermosetting rather than thermoplastic. This was confirmed when the condensation product, as expected, was found to be infusible even at temperatures of 400 ° C. In the preparation, usually two mols of formaldehyde were used because the product obtained was more porous and had a higher capacity.

Because of the scarcity of information on these resins, experiments were first carried out to determine whether the process taking place when ions were taken up by the resin was physical or chemical in nature. That the process is chemical was shown by the fact that titrations of the effluents indicated that precisely an equivalent of hydrogen ion was liberated for each equivalent of metal taken up by the resin. Data confirming this fact were obtained on silver, lead, and copper solutions.

To determine the capacity of the resin, the solution to be treated was allowed to flow at a fixed rate through a bed of the resin until analytical tests of the effluent showed metal ion concentrations of 10 p.p.m. to be coming through. This 10 p.p.m. is an arbitrarily chosen figure. Actually, until the resin approached saturation the concentrations were far below this, and as soon as 10 p.p.m. appeared in the effluent, the concentration rapidly rose to that of the feed solution.

A large series of experiments were then made, principally with acidified solutions of lead acetate, cupric chloride, bismuth nitrate, silver nitrate, etc., to fix the operating capacities of the resin as a function of particle size, the rate of flow and the concentration of the solutions. These results can be briefly summarized by saying that the capacities rapidly increased as the particle sizes and rate of flow decreased.

As an illustration of the results obtained, it was found that one pound of 65 to 100 mesh resin, operating at a superficial velocity of 2.5 cm./min. (2.5 cm^3/cm^2 empty tube cross sectional area) will adsorb 0.33 lbs. of lead or 0.43 lbs. of bismuth from a .0035 molar solution. This means that about 30% of all the hydroxyl groups in the resin sample had reacted with the bismuth. Considering the relatively large size of the particles, and the small surface area, this indicates that this resin is quite porous and that the metallic ions go fairly far into the structure of the particles.

The pH of the solution is very important in determining the amount of metal ion adsorbed. For example, twenty times more copper ion is adsorbed at a pH of 5.3 than at pH = 1.1. On the other hand, bismuth is retained by the resin in large amounts, 0.47 pounds per pound of resin, even at a pH of 1.0. Of course the effect of acidity is the basis of the recovery process which is carried out with 5% acid so as to reverse the equilibrium $RH + M^+ = RM + H^+$. The resin, however, will not stand up under alkaline conditions: 0.01 normal sodium hydroxide will soften and gradually dissolve the resin, giving a dark red solution.

The recovery of the adsorbed metal from the resin is quite complete and our data show that repeating the processes of saturation and regeneration results in no noticeable decrease in the capacity of the resin.

From an engineering and economic point of view, not nearly enough information is available on these new products to accurately predict which are the best and what are their probable future uses and value. Each type of resin in itself presents quite a problem in determining the optimum conditions for preparation and for operation. The cost of raw materials certainly is an important factor, particularly in the case of these polyhydroxy benzenes which at present have but a very limited market and do command a relatively high price. For this reason, similar products obtained by the condensation of formaldehyde with tannins and by the action of acids on coal are also very much worth while investigating.

Many possible uses suggest themselves for these resins besides water treatment. The recovery of valuable metals from reaction solutions or from mine waters: the removal of interfering metals present as traces in pharmaceuticals, dyes, extracts, etc., and possibly the separation of metals for analytical purposes. These resins can be expected to find in the future many applications not only in industry but also in the research laboratory.