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256 VANDERPOOL STREET
NEWARK. NEW JERSEY

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PIGMENT COLOR RESEARCH REPORT

ION EXCHANGE RESINS: APPLICATION TO COLORED PIGMENTS

Period Covered: December 1, 1945 to February 20, 1946

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PIGMENT COLOR RESEARCH REPORT

Final Report

Title: ION EXCHANGE RESINS: APPLICATION TO COLORED PIGMENTS

Period Covered: December 1, 1945 to February 20, 1946

SUBMITTED BY: Maxime Mac Kenzie
J. O. Morrison

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INTRODUCTION

Application of synthetic ion exchange resins has constantly expanded since their introduction in 1935 by Adams and Holmes (1). The unique properties of ion exchange resins, such as permitting efficient exchange of one ion for another without the necessity for forming a precipitate with subsequent filtration, or, in the case of particular resins, allowing adsorption of entire molecules, have led to constantly expanding use of these materials. The resins have been applied to such problems as: preparation of colloidal dispersions (without peptization and dialysis); recovery of valuable elements from waste solutions, as in the recovery of copper from plating solutions; purification of sugar solutions and other edible compositions; removal of unwanted salts from various chemical systems; and various separation processes and analytical procedures.

An investigation of ion exchange resins was undertaken with the intent of developing possible applications to the pigment industry. This report presents the program of study drawn up as the result of a literature survey, and briefly discusses the very limited experimental program carried out to date.

SUMMARY AND CONCLUSIONS:

The investigation of ion-exchange resins and of possible applications of these materials to colored pigments was initiated with a survey of the available literature.

Due to interruption of the program at an early date by another problem, quantitative experimental work was very limited. This consisted primarily of study of several comparatively salt-free sols; a few experiments on flocculating iron blues and a molybdenum blue colloid were also conducted. No positive leads were developed but further study is recommended.

DISCUSSION

Mechanism of Ion Exchange

Ionic exchange is usually defined as the interchange of ions between a liquid phase and a solid, resulting in no radical change in the structure of the solid. (Several cases of exchange between two solids in aqueous suspensions have also been reported.)

Ionic exchange can be of the following types:

Cation Exchange

1. Salt exchange in which one metallic or organic cation is replaced by another.

$$Ca^{++} + Na_2Z \qquad 2Na^{+} + CaZ \qquad \text{(Z = Cation Exchanger)}$$

2. Hydrogen cycle in which metallic or organic cations are replaced by hydrogen ions.

$$2Na^{+} + H_2Z \qquad 2H^{+} + Na_2Z$$

Anion Exchange

1. True Anion Exchange.

$$SO_4^{=} + 2(R_2NH)\,Cl \qquad 2Cl^{-} + (R_2NH)_2\,SO_4$$

(R_2N = free anion exchanger.)

2. Acid removal by addition.

$$HCl + (R_2N) \qquad (R_2NH)Cl$$

Ion exchangers, frequently, show marked selectivity which is controlled by such factors as electric charge, size, and concentration.

Proposed Investigation:

The original program of the present investigation included proposed study of the following applications of ion exchange resins:

1. Preparation of colloidal dispersions of various oxides, such as silicon dioxide, aluminum oxide, and titanium oxide, by ion exchange methods and study of these sols as possible lake-formers or precipitants for various dyes. Through insolubilization of the dyes, by addition of colloidal dispersions, it was hoped that pigments of unique properties, e.g. high strength, could be prepared.

2. Preparation of a pigment-type chromium (III) oxide through use of the resins. The present commercial method of preparing pigment-grade chromium (III) oxide is a rather expensive procedure involving, first, calcination of a mixture of a chromate or dichromate with boric acid or a phosphate, quenching the fused mass in hot water, grinding, and washing. Although the more intense forms of the pigment are believed to be hydrated oxides, the desired pigment properties are not obtained by direct precipitation of the hydrous oxide from chromic salt solutions. The difficulty of obtaining the desired product by precipitation methods may be associated with the fact that precipitated materials often contain a considerable quantity of foreign ions, whose removal if very difficult. It should be possible to prepare hydrated chromic oxide with only infinitesimal amounts of impurities by the ion exchange method. It was proposed to study the pigment properties of such material.

3. Recovery of valuable elements from waste solutions and evaluation of the costs of recovery. Concentration of dilute solutions of electrolytes has been effected through the use of ion exchange resins in many cases.

4. Treatment of pigments with hydrous oxide sols prepared through the use of ion exchange resins. Certain pigments are treated with various oxides, formed by precipitation in the presence of the pigment. Use of colloidal dispersions of the oxides for these treatments should be investigated.

5. Preparation of molybdenum blue precipitates by treating negatively charged molybdenum blue sols with positively charged hydroxide sols of metals like Al, Fe, Cr, Th, Sr, and Ce. Preparation of both types of sols normally involves dialysis. [illegible] procedures, [illegible]

dialysis. Ion exchange procedures, if applicable, would eliminate the time-consuming dialytic methods, and also result, presumably, in "purer" sols which might have improved pigment properties. Also, it was proposed to study direct preparation and simultaneous purification of the above sols by ion exchange methods, some success along these lines having been reported by J. W. Rymar (2).

6. Removal of excess salts from iron blue pigments through application of ion exchange procedures.

7. Improvement of zinc yellow for use in metal-protective primers. Removal of the undesirable ions (eg. chloride, sulfate) might be effected through purification of the ingredients used in certain zinc yellow processes or possibly through incorporation of a minute amount of an ion exchange resin into the zinc yellow.

8. Preparation of a silica sol, comparatively free of salts, by use of ion exchange resins. Some work has been done along these lines by Rymar (2). He prepared a silica sol of pH (6.0 - 6.3) which is near the 6.8 pH of the very pure sol formed by hydrolysing silicon tetrachloride. The colloidal solution was made from sodium silicate and sulfuric acid. The salts were removed by passing the solution through a cation-exchanger and then an anion-exchanger resin.

This salt-free silica sol might be applied to various pigments (e.g. phospho-tungstic or phospho-molybdic types) with the expectation of possible improvement in lightfastness, and, perhaps, variation of the particle size and surface of the pigments.

Some trouble has been had occasionally with pigments absorbing moisture too readily during storage. It is proposed that a small amount of salt-free silica be incorporated into such pigments. The moisture might then be adsorbed specifically by the silica, rather than by the pigment as a whole and the dispersing properties might be favorably altered.

Experimental

Four resins were chosen for laboratory use: De-Acidite (anion exchanger) and Zeo-Karb-H (hydrogen cycle-cation exchanger) both obtained from Permutit Company, 330 West 42nd St., New York, also Amberlite IR-300-H, (cation exchanger), and Amberlite IR-4 (anion exchanger), obtained from The Resinous Products and Chemical Company, Washington Square, Philadelphia. The Duolite resins were not used; available information (3) indicated that they might have slightly different characteristics than the four listed above.

Sufficient time was not allowed for study of variables effecting the stability of sols prepared by intimately mixing a given salt solution with the proper resin and then decanting the sol from the solid resin particles. The sols that were stable when prepared by hand agitation of the salt solution with resins (on a small scale) were not stable when prepared in larger amounts and stirred more thoroughly and over a longer period of time.

The use of these unstable solutions as flocculating or treating agents for soluble dyes or pigments is not a valid test of the effectiveness of comparatively salt-free sols, for, upon precipitation, the charge on the colloidal sol particles is diminished and their flocculating capacity is correspondingly decreased. This

limitation must be considered in interpreting the experimental results which, briefly, were as follows:

(1) Dilute solutions of aluminum chloride, aluminum sulfate, chromium chloride, chromium sulfate, titanyl sulfate, cobalt chloride, nickelous chloride, nickelous sulfate, and copper chloride were treated with De-Acidite in attempts to prepare sols of the respective oxides. Analyses of the resulting solutions showed a substantial removal of the anions.

(2) Sols of aluminum oxide were prepared by removing the anions from solutions of aluminum sulfate or aluminum chloride by use of the anion exchanger, Amberlite IR-4-B. These sols were used in attempts to precipitate Peacock Blue Lake BL-72-D, normally manufactured by ~~Lithosol~~ leking Brilliant Blue E Dye on alumina hydrate (prepared from aluminum sulfate and sodium carbonate). Very little precipitation occurred when the sols of aluminum oxide were added to the Blue. It has not yet been determined whether the unsatisfactorily slight precipitation was due to the relative instability of the sol or to possible similarity of electrical charges of the dye and sol.

(3) Treatment of a chrome yellow with aluminum oxide sols of the above type gave no improvement in pigment properties over the standard Chrome yellows. (Instability of sols may be the cause of negative results).

(4) Settling rates of iron blue slurry treated with aluminum oxide sol (aluminum sulfate + Amberlite IR-4-B) showed no improvement over those of untreated blue slurry (stability of sols possibly at fault). A fairly stable sol was prepared from copper acetate in a like fashion. This sol apparently did increase the initial settling rate of the iron blue slurry.

(5) A sol prepared from aluminum chloride and Amberlite IR-4-B flocculated a molybdenum blue sol.

POSSIBILITES FOR FUTURE WORK

(1) Data needed for successful preparation of sols must be obtained experimentally; there is very little of this information in the literature. The variables (time of agitation of the solution with the resin, temperature, concentration of solution, ratio of salt to resin) must be studied for each salt; all are critical variables in sol formation. The extent of hydration of the resins must be known in order to establish the ratio of salt to "active" resin.

(2) The balance of the program as originally outlined (Page 2) should be investigated.

(3) Study of the flocculating action of aluminum oxide sols (4) and hydrous ferric oxide on iron blues (5) might be of value.

(4) Most pigments must be washed free of salts before being dried. Therefore, use of salt-free sols would be advantageous, the washing step being decreased or eliminated when the sols are used as flocculating or treating agents for pigments, (e.g., in the preparation of the blue lake BL-72-D).

(5) The use of the resins should be studied to obtain the highest exchanger capacity (6) (7) and the fastest exchange conditions.

(6) Processes in which ion exchange occurs between two solids in suspension (8) (9) are of interest.

(7) Preparation of a sol of an exchange resin that would retain its exchange properties in the sol state.

(8) Organosols of pigments might be made and flushed directly into organic vehicles. These sols could be prepared through ion-exchange (employing the slight amount of water that is required for the ion exchange) or by other methods.

In the course of the ion exchange program, the importance of true colloidal solutions in the pigment field became quite apparent. Colloids, because of the active charge on the colloidal particles, should logically be more powerful lake-formers than salt solutions. Wider investigation of the use of true colloids in pigments should be encouraged (10).

PATENT SITUATION:

Numerous patents on ion exchange processes have been issued; there appears to be a constant increase in their number. A patent application by Rohm and Haas (Brit. Appl. 22585, Nov. 15, 1944) outlines a process for acidifying certain silicates (which form gels in acid medium) without destroying the gel structure of these materials. A slurry of the silicates is mixed with a cation exchanger (hydrogen cycle); separation is effected by mechanical means. By analogy it might be possible to remove acid from pigment slurries by using an anion exchanger (e.g. De Acidite), thus retaining the structure of the gels which is often destroyed by ordinary neutralization.

EXPERIMENTAL DETAILS:

See Notebook 1183.

REFERENCES:

Reference (12), below, presents a comprehensive (209 page) compilation of abstracts of literature covering scientific and industrial application of ion-exchange materials. This was published subsequent to termination of the study reported herein.

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2. J. W. Ryznar, Ind. Eng. Chem. 36, 821, 1944

3. C. S. Moore, Jr. (Industrial Engineering Division), letter to C. W. Balch, Jan. 23, 1946.

4. H. B. Weiser, The Hydrous Oxides.

5. Holtzmann, Ind. and Eng. Chem., Vol. 37, p. 856, September, 1945.

6. U. S. Patent 2,376, 914; Zeolite Regeneration.

7. British Patent: 573, 814, Modification of the Relative Concentration of Cations in Fluid Media.

8. British Patent Application, 16598, Treatment of gel-forming hydrous silicates.

9. British Patent Application, 22585, Stable, gelling, acidic hydrous silicates.

10. Hydrous Oxides by Ion Exchange Techniques.
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11. Ionic Exchange, (Memorandum to Dr. P. L. Salzberg from Norman G. Fisher, and Martha M. Duffey), Experimental Station, October 5, 1945, DuPont.

12. Ionic Exchange, L.S.X. 1683, Martha Duffey, Chem. Dept. Experimental Station, DuPont, May 1946.