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3,434,864

SENSITIZED SHEET MATERIAL CONTAINING DE-AMMONIATED, AMMONIUM-EXCHANGED MOLECULAR SIEVE

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8 Claims

ABSTRACT OF THE DISCLOSURE

A crystalline zeolitic molecular sieve having uniform pore openings within the range of 3 to 15 angstrom units is ion-exchanged with ammonium ions and is then thermally treated at elevated temperature until ammonia is removed. The resulting zeolite is employed as a reactive pigment in receiving sheets for printing with color-reactant leuco dye material.

This invention generally relates to pressure-sensitive record material of the type utilizing multiple colorless, color-reactant materials which produce a colored mark upon adsorptive contact with each other, as exemplified by the manifold record material described in U.S. 2,730,456 to Barrett K. Green and Lowell Schleicher. More specifically, this invention has to do with an improvement in the sensitized color-reactable pigment member of the pressure-sensitive record material which serves as the print-receiving surface in conjunction with a printing fluid comprising normally colorless, color-reactable organic material that is converted to its colored form upon adsorptive contact with the sensitized pigment.

A type of manifold printing record material which obviates the use of carbon paper is produced by coating sheet material with a multiplicity of pressure rupturable microscopic capsules of a printing fluid comprising an oily vehicle and at least one normally colorless color-reactant organic material which turns to colored form upon contacting sheet material which has been properly sensitized. The manifold record material is assembled for manifold printing by stacking sheet material coated with encapsulated color-reactant organic material in face-to-face relationship with a sensitized coating on another sheet. Upon rupture of the capsules containing color-reactant material, as by writing, typing or printing pressure, the color-reactant organic material comes into adsorptive contact with the sensitized coating and produces a mark. As in the production of other record forming material, the ultimate objective in formulating the constituents making up this type of record forming material is to obtain a very white printed sheet in which the print is registered accurately as uniform contrasting dark or colored marks which clearly stand out from the white background.

One of the most practical forms of a manifold printing system of the type described above involves the use as the printing fluid of an encapsulated oily mixture of two particular color-reactant organic materials, namely, crystal violet lactone (3,3 bis(p-dimethylaminophenyl) 6-dimethylaminophthalide) and benzoyl leucomethylene blue. The crystal violet lactone produces a blue mark substantially immediately upon coming into adsorptive contact with a properly sensitized receiving sheet. This mark however, is not permanent, and it disappears in time. The benzoyl leucomethylene blue develops more slowly and forms a substantially permanent blue mark before the

initially formed mark fades. Therefore, a dark blue mark is present at all times after printing pressure is applied to the coating.

The clay material that is commercially used in forming the sensitized print-receiving sheet when printing with the mixture of crystal violet lactone and benzoyl leucomethylene blue is calcined attapulgite clay. This particular type of clay is mixed with about 10% by weight of finely divided precipitated silica pigment. The combination of pigment materials results in a coated receiving sheet which is exceptionally sensitive to a normally colorless mixture of crystal violet lactone and the leuco form of methylene blue. Therefore, sheet material coated with the mixed pigments acquires both a temporary and permanent dark blue color upon coming into adsorptive contact with the dye mixture.

The appearance of a receiving sheet sensitized with the attapulgite clay mixture leaves much to be desired since the attapulgite clay coated sheet does not approach the whiteness of present day high-grade coated-paper stock. This is because attapulgite clay is of itself a yellowish material and it cannot be brightened appreciably without destroying its intrinsic sensitizing character. The G.E. brightness of the commercial sensitized receiving sheet made up with an attapulgite clay coating is only about 65% to 70% as compared to brightness values of 85% to 95% or more for paper stock coated with high grade kaolin clay, a very white clay material. While it might therefore appear to be a logical expedient to use kaolin clay, which is a very white clay in forming the sensitized coating for manifold record material when using crystal violet lactone and the leuco form of methylene blue as the printing fluid, this is not a satisfactory alternative. Kaolin clay, although it is an acid clay, is relatively insensitive to both crystal violet lactone and to the leuco form of methylene blue. As a result, only a very weak blue mark is obtained upon transfer of either of these materials to a sheet coated with kaolin clay. The mark is considerably too weak for practical usage and does not compare favorably with the intensity of the mark obtained with attapulgite clay.

Accordingly, it is an object of this invention to provide a highly sensitive receiving sheet of improved whiteness or brightness.

A more specific object is to provide white sensitized receiving sheets which register intense blue marks upon transfer of leuco dyes such as crystal violet lactone and benzoyl leucomethylene blue.

Further objects and advantages will be apparent from a description of this invention which follows.

This invention is a result of a surprising and unexpected discovery that a specific type of crystalline zeolite, known as a molecular sieve, when ion-exchanged with ammonium ion and then thermally deammoniated at elevated temperature, produces remarkable results when employed as a white pigment in the preparation of sensitized sheets for printing with color-reactant organic printing fluids.

The white pigment which is used to coat and/or fill sheet material, in accordance with this invention, is a finely divided crystalline zeolitic aluminosilicate obtained by ion-exchanging a metal aluminosilicate having uniform pore openings between 3 to 15 angstrom units with ammonium ions, followed by thermal treatment at a temperature within the range of about 650° F. to 1,200° F. for a time sufficient to eliminate substantially completely the ammonia. The crystalline zeolites that are employed as starting materials in the preparation of the pigment are usually referred to as "molecular sieves." These sieves are usually identified by means of a letter. Among the molecular sieves may be mentioned the crystalline zeolites re-

ferred to in the patent literature as A, Y, L, D, R, S, T, Z, E, F, Q, B, X, ZK-4, Zeolite-alpha and ZK-5. Reference is made to U.S. 3,140,249 and U.S. 3,140,251 both to Plank and Rosinski. These patents include description of methods for preparing and identifying some of these crystalline zeolites. Crystalline molecular sieves are usually identified by standard X-ray diffraction techniques since each sieve has a characteristic X-ray diffraction pattern.

The sensitivity of calcined, deammoniated ion-exchanged zeolite pigments towards a mixture of crystal violet lactone and benzoyl leucomethylene blue differs substantially from the sensitivity of the parent crystalline zeolite before or after ion-exchange with ammonium ion. The calcined deammoniated exchanged zeolite is also more sensitive than kaolin and, in fact, is more sensitive than the attapulgite clay that is used commercially in sensitized coatings. Transfer of a mixture of crystal violet lactone and benzoyl leucomethylene blue into contact with a sheet coated with calcined deammoniated zeolite, in accordance with this invention, results in an immediate and permanent intense true blue coloration at the site of adsorptive contact. On the other hand, upon adsorptive contact of a mixture of these organic printing fluids with the parent metal aluminum silicate zeolite or calcined metal aluminum silicate zeolite, only weak marks result. Surprisingly, the novel silicate pigment of this invention is no more acid (as determined by pK_a tests) than kaolin clay or attapulgite clay. Therefore, the superiority in sensitivity of the calcined ammonium ion-exchanged zeolite over these other silicate materials cannot be accounted for on this basis.

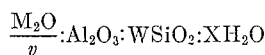
Paper coated or filled with the crystalline calcined deammoniated exchanged zeolite pigment of this invention is considerably whiter than paper coated or filled with attapulgite clay or a mixture of attapulgite clay and silica pigment. Whereas a representative sample of a commercial print-receiving sheet which has been coated with a mixture of attapulgite clay and silica has a G.E. brightness value of only 65% to 75%, paper coated with the novel silicate of this invention as the sole coating pigment has a brightness of 90% or more. Therefore, when a coated sheet of this invention is subjected to printing using a mixture of benzoyl leucomethylene blue and crystal violet lactone, the printed record is a very white sheet containing clear dark blue markings which stand out from the background.

The method for producing the sensitized crystalline ion-exchanged zeolitic pigments employed in the practice of this invention and the application of the pigment to manifold printing will be more fully understood by the following detailed description thereof.

THE PIGMENT

(a) The metal aluminosilicate precursor of the pigment

As mentioned above, the metal aluminosilicate precursors of the pigment used in the practice of this invention, constitute a specific type of crystalline zeolite. These metal aluminosilicates contain varying quantities of metal (usually alkali metal) atoms, silicon, aluminum, and oxygen arranged in the form of an aluminosilicate salt in a definite and consistent crystalline pattern. The crystals contain a greater number of small uniformly sized cavities interconnected by smaller uniformly sized channels. The alkali metal aluminosilicates have uniform pore structures characterized by having an effective pore diameter between 3 to 15 angstrom units. The structural formula of the metal aluminosilicates is as follows:



wherein M is a metal cation, v is the valence of M, W is a value from 2 to about 6 and X is a value up to about 9. These zeolites can be prepared, for example, by heating an aqueous solution containing mixtures of oxides, especially mixtures of Na_2O , Al_2O_3 , SiO_2 and H_2O , at about

100° C. until crystals are formed; the zeolite crystals are separated, washed and then, if desired, dehydrated.

For economic reasons, it is preferred to use a crystalline alkali metal (especially sodium) aluminosilicate zeolite as the starting material in producing the ammonium exchanged zeolite. However, alkali metal aluminosilicates having uniform pore openings within the range of 3 to 15 angstrom units may be ion-exchanged, partially or substantially completely, with any of the following before being exchanged with ammonium ion: hydrogen, metals of groups II-A, III-B and IV-B of the Periodic Table.

(b) Ion-exchanging the zeolite with ammonium ion

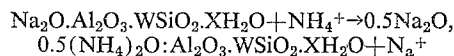
The zeolite that is ion-exchanged with ammonium ion can be used in fully hydrated, partially dehydrated or substantially fully dehydrated form, provided the dehydration has been carried out at a temperature below which the crystal structure of the zeolite is destroyed to an appreciable extent.

Any soluble ammonium salt can be used to ion exchange the cation of the zeolite provided the salt formed during the ion exchange is soluble. Since most crystalline zeolites of the required type are synthesized in the alkali metal form, and since most alkali metal salts are as soluble as ammonium salts, practically any soluble ammonium salt can be used. When, however, the zeolite has been exchanged with other ions, such as calcium, before being exchanged with ammonium ion, the anion in the ammonium salt must be selected with more care. Ammonium chloride, nitrate, sulfate, sulfite, acetate, or other ammonium salts can be used in most cases, as can salts containing quaternary ammonium cations such as tetramethylammonium cation.

Before ammonium ion-exchange, the zeolite can be washed with acid provided the zeolite crystals are not decomposed by the acid treatment used. The acid treatment removes undesirable impurities that may be present.

The ion-exchange can be carried out on a continuous basis by passing a solution containing ammonium ions over the zeolite and continuously removing the effluent. Batchwise exchange can also be effected by slurrying the zeolite in the solution containing ammonium ion and maintaining the zeolite in contact with the solution until a desired amount of exchange is effected. The exchange is usually favored by maintaining the exchange solution at about 175° F. to 210° F. The amount of exchange can be within the range of about 25% to 100%, whereby the ammonium ion constitutes from 25% to 100% of the exchangeable cations.

The reaction which occurs can be summarized by the following equation, illustrating partial exchange:



The ammonium exchange results in a very small change in the crystal structure of the zeolite, as evidenced by a small change in the peak intensity of the characteristic diffraction lines on the X-ray pattern. The peaks present in the pattern of the sodium form of the zeolite are the same peaks present in the pattern of the ammonium exchanged form. The crystals can be water-washed after exchange with ammonium ion, if desired.

(c) Calcination of ammonium exchanged zeolite

The ammonium exchanged zeolite is calcined at a temperature within the range of about 650° F. to about 1,200° F. until substantially no more ammonia gas can be given off from the zeolite. The calcination is carried out in air which aids in removing ammonia gas. The pressure can be atmospheric or reduced pressure can be employed. The calcination can also be carried out in an atmosphere of 30% to 100% steam at about 750° F. to 850° F.

The zeolite pigment has substantially the same X-ray diffraction before and after the calcination, although it is within the scope of the invention to use calcined am-

monium ion-exchanged zeolite which has an X-ray diffraction pattern altered somewhat as a result of calcination following ammonium ion-exchange.

The calcined ammonium exchanged zeolite is substantially anhydrous. However, the material, like the parent sodium zeolite, is readily rehydrated. If desired, the calcined exchanged zeolite can be rehydrated, partially or completely, by addition of water or steam. At any rate, the zeolite will be rehydrated in situ when formulated into an aqueous coating or filler composition.

The calcined material is crushed and milled to a suitable size for use as a pigment, e.g., to an average particle size of 10 microns or finer.

FORMATION OF SENSITIZED COATED SHEET MATERIAL

Color-reactant sensitized sheet material is made up by applying an aqueous dispersion of the finely divided calcined ammonium exchanged zeolite to at least one surface of a suitable sheet material, usually paper. A water-dispersible adhesive such as starch, styrene-butadiene, latex, casein or mixtures thereof, is incorporated with the aqueous dispersion as a binder for the pigment. Normally an alkali metal silicate pigment dispersant is also incorporated in the dispersion. Other dispersants, such as sodium salts of condensed phosphates (including tetrasodium pyrophosphate), etc., can be used. The pigment coating is uniformly applied to a base sheet by any of the familiar types of coating equipment. The coating is applied to the base sheet in amount such as to provide a uniform coat about 0.0005-inch thick. The base sheet is usually paper stock although other sheet material, such as, for example, glass, plastics or paperboard, may be employed inasmuch as the base material performs no active part in the printing process and serves merely as a carrier for the sensitized pigment.

While in the preferred form of this invention, calcined ammonium exchanged zeolite is the sole pigment used in forming the sensitized coating, other sensitized pigments, or even nonsensitive pigments, may be employed in conjunction with the calcined ammonium exchanged zeolite.

The calcined ammonium exchanged zeolite pigment coating constitutes the front surface of an improved manifold record material of this invention. The rear surface which forms the transfer coating of the sheet material is coated with a multiplicity of microscopic rupturable capsules containing oil, crystal violet lactone and benzoyl leucomethylene blue. In manifold printing, a plurality of these sheets are stacked in a manner such that the sensitive pigment coated surface of one sheet is in face-to-face relationship with a coating of rupturable encapsulated printing fluid of another sheet. In practice, the pigment coating is normally applied to the wire side of a sheet of raw stock and an emulsion coating containing printing fluid is applied to the felt side. Suitable transfer coating compositions and methods for producing a coating of a multiplicity of microscopic oil-containing encapsulated printing fluid are described in detail in U.S. 2,730,456 to Barrett K. Green and Lowell Schleicher. However, means for forming a coating of microscopic rupturable capsules other than the means described in said patent may be used since the sensitivity of the pigment is generally independent of the particular composition of the rupturable capsule shell containing the crystal violet lactone-benzoyl leucomethylene blue mixture.

A typical composition of encapsulated printing fluid comprises about equal weight proportions of crystal violet lactone and benzoyl leucomethylene blue dissolved in trichlorodiphenyl or other water-immiscible oil.

Also, in accordance with this invention, the sensitized zeolite pigment may be applied as a layer to a previously formed coating of encapsulated organic color-reactant materials or the latter may be applied directly over a layer of the pigment coating.

It is also within the compass of this invention to use the sensitized zeolite as a filler in the making of paper. The zeolite can be employed in the amount usually used when kaolin filler clay is used and is added to the paper stock before the stock is charged to the paper-making machinery.

The following examples illustrate the preparation of a sensitized calcined ammonium exchanged synthetic crystalline zeolite and its use in manifold printing with leuco dyes.

PREPARATION OF CRYSTALLINE SODIUM ZEOLITE

A sample of a crystalline sodium aluminosilicate zeolite having the X-ray diffraction pattern of sodium zeolite Y, as described in U.S. 3,130,007 to Breck, was prepared. The sample contained 74% by weight of sodium zeolite Y, as determined by the X-ray diffraction procedure described in U.S. 3,130,007 and had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 4.0, as determined by applying to an X-ray diffraction pattern of the product the criterion set forth in Table III of a publication by Donald G. Freeman, Jr., entitled "Electrical Conductivity of Synthetic Crystalline Zeolite," Journal of Chemical Physics, vol. 35, No. 3, September 1961. Table III of said publication correlates unit cell dimension with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

AMMONIUM NITRATE EXCHANGE OF ZEOLITE

About 50% of the Na^+ of the zeolite was exchanged with NH_4^+ as follows. Eight hundred and eighty-five grams of the sample of sodium zeolite was slurried with 2,000 ml. of 1 N aqueous ammonium nitrate solution. The slurry was filtered on a Buchner funnel and after an hour and one-quarter, 500 ml. of 0.1 N ammonium nitrate solution was added to the filter cake and the filtration resumed. After another hour an additional 500 ml. of 1 N ammonia nitrate was added to the cake and filtered. This procedure was repeated with 500 ml. portions of exchange solution until the Na_2O content of the zeolite was 3.22% by weight (based on the volatile free weight of the zeolite). The Na_2O content of the zeolite before ion-exchange was 13.3%, on a volatile free weight basis.

The ion-exchanged zeolite on the Buchner funnel was crushed in a jaw crusher, dried at 200° F. for 2 hours in a despatch oven and ground in a high speed hammer mill (Mikro-Pulverizer) through a 0.020-inch screen (1 pass). At this point, the zeolite had a B.E.T. surface area of 377 m^2/g .

CALCINATION OF AMMONIUM EXCHANGED ZEOLITE

The ammonium exchanged zeolite was calcined in a muffle furnace at 1,100° F. for 2 hours, producing a very white pigment.

PREPARATION OF ZEOLITE PIGMENTED COATING COMPOSITION AND COATING OF PAPER

Base sheets for color reaction with organic color-reactable printing fluid were produced with the calcined ammonium exchanged zeolite as the coating pigment. The composition of the coating composition was as follows:

Parts by weight	
Pigment (ammonium-exchanged sodium zeolite calcined at 1,100° F.)	100
Distilled water	299
"N" brand sodium silicate (37.6% solids suspension, $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 3.2:1)	20.2
Styrene-butadiene latex, 48% (Dow 512R)	50.0
Casein solution, 20%	2.5

The general procedure for preparing coating colors was as follows: cooked casein was soaked in water at approximately 20% solids for 10 minutes prior to the addition of 12% ammonium hydroxide. The temperature of the casein suspension was raised to 120° F. and maintained at that temperature for 10 minutes.

Sodium silicate (pigment dispersant) was added to the water prior to addition of zeolite pigment. The latex-casein mixture was added to the pigment suspension, thoroughly mixed and screened through a 100-mesh vibrating stock.

Sheets of raw paper stock were coated with the calcined ammonium-exchanged zeolite in amount to produce a coat weight of 5 pounds/3,000 square feet. The paper was coated in the machine direction on the felt side. The sheets were oven dried at 220° F. immediately after being coated, cut on a 6" x 10" die, placed in a photo print dryer with the coated side out for 3 minutes. The sheets were rapidly placed in a sealed polyethylene bag and stored in a closed drawer in a constant temperature and humidity room (73° F. and 50% R.H.).

EVALUATION OF SENSITIZED COATED SHEETS

The sensitivity of crystal violet lactone and benzoyl leucomethylene blue towards each of the coated sheets were determined by placing a commercial emulsion color-reactant coated paper containing encapsulated oil, crystal violet lactone and benzoyl leucomethylene blue directly over and into contact with the pigment coated sheet. The two sheets were simultaneously passed through a calender under pressure sufficient to rupture the microscopic capsules and liberate the printing fluid mixture.

Sensitivity was determined by contrasting the printed and unprinted areas of the sheet in accordance with a procedure of The National Cash Register Company entitled, "Process Specification No. 730.27, Section J, Subject: Paper and Printing." The results were compared with those obtained with present day commercial mixtures of attapulgite and silica gel.

Briefly, the testing involves calculating a "Calender Intensity" value which was determined by comparing the reflectance of the printed area with the reflectance of the background. A Bausch & Lomb opacimeter with a green filter (572 mu peak) was used. The formula was:

Percent calender intensity

$$= \frac{\text{Average printed area reflectance}}{\text{Average background reflectance}} \times 100$$

The percent calender intensity was determined 30 seconds after calendering and again 48 hours after testing. It can be seen that a low calender intensity value indicates a good contrast ratio.

CONTRAST RATIO OF PIGMENT COATED SHEETS
PRINTED WITH LEUCO DYES

Pigment	Time after calendering	
	30 Sec.	48 hr.
Calcined Ammonium-ion Exchanged Crystalline Zeolite	44	38
Attapulgite-Xyloid Mixture (9/1 weight ratio)	50-55	40-45

The results summarized in the table show that the paper sensitized with the experimental pigment had a markedly superior contrast ratio to the paper sensitized in accordance with present practice.

Visual comparison corroborated these results. The experimental coated sheet was more pleasing to the eye since the background was much whiter and the printed blue registered more sharply against the background.

We claim:

1. Sheet material containing sensitized color-reactable pigment particles obtained by ion-exchanging a crystalline metal aluminosilicate zeolite having uniform pore

openings between 3 to 15 angstrom units with ammonium ions, followed by thermal treatment at a temperature within the range of about 650° F. to 1,200° F. for a time sufficient to eliminate substantially completely ammonia therefrom.

2. The article of claim 1 in which the sheet material is paper.

3. The article of claim 2 in which said pigment is present as a surface coating on the paper.

4. The article of claim 2 in which said pigment is present as a filler in the paper.

5. Paper having coated on a surface thereof a sensitized color-reactable surface coating comprising a binder and crystalline zeolite pigment particles in amount sufficient to provide a white pigmented coating on said paper, said zeolite particles having been obtained by ion-exchanging a crystalline metal aluminosilicate zeolite having uniform pore openings between 3 to 15 angstrom units with ammonium ions, followed by thermal treatment at a temperature within the range of about 650° F. to 1200° F. for a time sufficient to eliminate substantially completely ammonia therefrom, said pigment particles being further characterized by producing an intense blue color upon being put into adsorptive contact with normally colorless crystal violet lactone and with normally colorless benzoyl leucomethylene blue.

6. Paper coated with crystalline sodium zeolite Y in which at least 25% of the sodium ions have been exchanged with ammonium ions and the exchanged zeolite has been deammoniated by calcination at a temperature within the range of 650° F. to 1,200° F.

7. Paper filled with crystalline sodium zeolite Y in which at least 25% of the sodium ions have been exchanged with ammonium ions and the exchanged zeolite has been deammoniated by calcination at a temperature within the range of 650° F. to 1,200° F. for a time sufficient to eliminate substantially completely ammonia therefrom.

8. A paper coating composition consisting essentially of (a) water, (b) pigment particles obtained by ion-exchanging a crystalline metal aluminosilicate zeolite having uniform pore openings between 3 to 15 angstrom units with ammonium ions, followed by thermal treatment at a temperature within the range of about 650° F. to 1,200° F. for a time sufficient to eliminate substantially completely ammonia therefrom, (c) a compound capable of dispersing said pigment in the water and (d) a water-dispersible adhesive selected from the group consisting of starch, styrene-butadiene latex, casein and mixtures thereof.

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