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2,918,399

STEREOTYPE DRY MAT

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This invention relates to improvements in stereotype mats and particularly to a stereotype dry mat having improved plasticity when moist whereby the molding and casting properties thereof are improved. The invention also relates to the method of improving the molding and casting properties of a stereotype dry mat.

A stereotype dry mat is a highly specialized sheet-form product comprising co-felted cellulose fibers and a filler, which is plastic in the moistened conditioned whereby it is adapted to take a deep and well-defined impression from a printing form and, after being separated from the form and dried, is capable of producing many duplicates or stereotypes of the printing form by casting molten stereotype metal against the molded stereotype dry mat and allowing the metal to cool and solidify. The stereotype dry mat makes it possible to obtain a number of metal printing surfaces, containing type and illustrations, from a single original metal form.

The present invention relates to a stereotype dry mat which, as stated heretofore, conventionally comprises a thick sheet of co-felted cellulose fibers and discrete particles of a filler. The fibers are composed of rag stock, cotton linters, wood fibers, such as alpha, sulfite, soda pulp fibers, or the like and the filler, in accordance with known practice, is composed of powdered clay, talc, or the like. An aqueous slurry of a mixture of the fibers and filler is prepared in a beater, and the mixture is felted upon the screen of a paper-making wet machine to form a web. The web is then transferred to a moving endless felt and thence to a revolving roll, and the web is wound upon the roll until a sufficient number of layers has been accumulated to form a mat of the desired thickness. The wet mat is then removed from the roll and dried.

During the drying operation, the face of the mat, which is the surface into which the metal printing form will be impressed, is calendered so that such face is rendered smooth and free of projecting fibers, while the back of the mat is usually maintained against a porous surface such as a woven fabric felt. As a result of such operation, the surface of the back is maintained porous and irregular, relative to the face, and the moisture escapes readily from the back. In customary practice, the thickness of a finished stereotype dry mat is from .015 inch to .060 inch.

For the purpose of facilitating the separation of the solidified metal plate from the stereotype mat after the casting operation, a release-promoting coating may be applied to the face of the mat. A suitable composition for this purpose is disclosed in United States Patent No. 1,863,731.

After the stereotype mat has been formed as described, it is made ready for use by moistening it with water. In customary practice, the moisture content is controlled so as to be approximately 7 percent to 50 percent, based on the weight of the moistened mat. In this moistened condition, the mat is plastic and the printing form, containing the type, cuts, halftones, etc., is impressed against the face of the mat whereby the latter takes a deep and

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well-defined impression of the form. For this operation, the greater the plasticity of the stereotype mat the more excellent is the impression in that it is deeper and more sharply defined, especially in the fine details, halftones, etc., and the principal contribution of the present invention is that the mat thereof is characterized by high plasticity when moist.

After the impression has been made upon the mat, the latter is dried by subjecting it to heat in drying apparatus which is called a "scorcher." It is essential that the moisture be driven out rapidly and completely without rupture of the mat, and the mat of the present invention possesses the essential property of permitting the rapid and complete escape of moisture.

After the mat has been thoroughly dried, it is ready for the casting operation and for this purpose is placed in a casting box. The impression from the printing form is made while the mat is in the flat condition, but since printing is usually carried out by cylindrical presses, before casting the mat is curved to conform to the shape of the presses and is placed in a curved casting box. In the casting box, the molten stereotype metal is flowed against the face of the mat, and the metal is allowed to cool and solidify, after which it is separated from the mat.

From the performance standpoint, a stereotype dry mat must be capable of taking a substantial number of casts, as many as thirty being not unusual. It is, therefore, of greatest importance that the face of the mat be smooth and tough and free of surface roughness or projecting fibers. If it is not, the molten metal will flow into the surface roughness or around the projecting fibers and the cast metal plate will adhere to the mat and when it is separated therefrom will carry with it portions of the surface of the mat or tear loose the projecting fibers. If any such action occurs the surface of the mat is impaired for taking additional casts and the usefulness thereof is at an end.

In addition to the properties which have been described, for successful performance, the stereotype dry mat should shrink uniformly and the desired amount when it is dried from the moistened condition. It must also be flexible when dried so that it will conform readily to the curved shape of the casting box. At the same time it must possess sufficient strength that it will resist the pressure of the cast metal and will not be compressed thereby, which would cause a loss of depth of the characters of the cast plate. The mat must also be tough and highly resistant to the heat of the molten metal. Even the slightest decomposition of the mat due to heat will cause impairment of the surface of the cast metal plate and render it unsuitable for use. The mat of the present invention possesses all of these properties and renders superior performance in the casting of metal plates.

It is the principal object of the invention to provide a stereotype dry mat possessing superior plasticity when moist, whereby a deep and well-defined impression is taken from the printing form with a minimum of pressure. As a further result, cast printing plates are obtained from the mat which are superior reproductions of the original printing form. As an additional result of the superior plasticity, the face of the mat is smooth and free of projecting fibers and a large number of cast plates are obtained from a single mat without impairment of the casting properties thereof.

Another object is to provide a stereotype dry mat which shrinks uniformly and the desired amount when dried from the moist condition and at the same time possesses the strength desired in a stereotype dry mat.

It is a further object to provide a stereotype dry mat having the other desirable properties described hereinbefore, including the ready release of moisture during

drying, and strength and flexibility in the dry condition.

Other objects and advantages will become apparent as the following description progresses in which a number of embodiments of the stereotype dry mat of the invention are described.

Briefly, the objects of the invention are realized by incorporating as an essential ingredient of the filler of the mat, in partial or complete replacement of an ordinary filler such as clay or talc, a synthetic inorganic zeolite gel. Synthetic inorganic gel zeolites are known and are used for cation exchange purposes in the field of water treatment, especially water softening. An example of such a zeolite is the product formed by reacting sodium silicate and sodium aluminate or aluminum sulfate in aqueous solution, which product is generally called sodium aluminum silicate and sometimes called the double silicate of sodium and aluminum and designated by the formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2$. This zeolite has been found to be a satisfactory filler in accordance with the present invention.

In addition to the sodium zeolite, which is formed by reacting sodium silicate with a soluble metal compound, the corresponding potassium zeolite is suitable, which is formed by reacting potassium silicate with a soluble metal compound. Zeolites which are formed by reacting a water soluble silicate, i.e., sodium silicate or potassium silicate, with a water soluble compound of an amphoteric metal other than aluminum, such as zinc, lead, tin, iron, chromium, titanium, manganese, molybdenum, and the like are also suitable for use as a filler for stereotype dry mats in accordance with the present invention. Also, the cation exchange products of the sodium and potassium zeolites which have been described are satisfactory for such use. Such exchange products are formed by cation exchange with other cations, such as calcium, magnesium, ammonium and the like. Such cation exchange is effected by passing in contact with the sodium or potassium zeolite water containing dissolved therein compounds of such other cations, such as the chlorides, sulfates and carbonates of calcium and magnesium, and other compounds capable of undergoing cation exchange. As an example, in such exchange operation, the calcium of the calcium chloride replaces the sodium or potassium of the zeolite. The resulting calcium zeolite is satisfactory for use as a filler in accordance with the invention.

In general, the zeolite which is suitable is the inorganic gel reaction product of a water soluble alkali metal silicate and a water soluble compound of an amphoteric metal, and the cation exchange products of such reaction product, such products being the synthetic gel double silicate of sodium or potassium and the amphoteric metal and the cation exchange products of such double silicate. The term "pre-formed synthetic" as used herein and in the claims with reference to the inorganic gel zeolites is used to describe the double silicate filler which is produced prior to its incorporation into the cellulose fiber slurry, as contrasted to double silicate fillers which are produced by a reaction of its ingredients within the cellulose fiber slurry.

Natural zeolites, such as those known as greensand or glauconite, are not suitable for the purpose of the invention, the zeolite contemplated by the invention being the pre-formed synthetic inorganic gel zeolites and the cation exchange products of such zeolites.

In the final stereotype dry mat, the synthetic gel zeolite filler is in the form of discrete particles. The size of the particles is not critical, the same size as is customarily used with ordinary clay or talc fillers for stereotype dry mats being suitable. In the preferred procedure for making the mat, the zeolite is ground to a powder, but this is not necessary because the zeolite is soft and frangible, and lumps which may be present are readily broken down in the mixing of the fibers and filler which occurs prior to the felting of the mixture into a sheet.

The proportions of the synthetic inorganic gel zeolite in the stereotype mat are not critical and may be varied within relatively wide limits. When it is used in admixture with other fillers, as little as 1.0 percent produces a substantial beneficial effect in improved plasticity when moist. When used alone, approximately 2.5 percent to 50 percent produces satisfactory results for the purpose of imparting improved plasticity and improved molding and casting properties to the mat. The proportions of zeolite filler given herein, in the specification and claims, are on a weight basis, the amount of the zeolite being in terms of the weight of the zeolite, exclusive of water of hydration, and the weight of the stereotype mat being in terms of the weight of the fibers and filler, exclusive of uncombined water.

To provide a better understanding of the invention, a number of examples of the preparation of a stereotype mat in accordance with the invention are given in the following. It is to be understood that these examples are by way of illustration and that variations therefrom may be made by those skilled in the art. In the examples, all proportions are on a weight basis.

Example 1

45 parts of sodium silicate having the ratio
 $1\text{Na}_2\text{O}:2\text{SiO}_2$

is dissolved in 450 parts of water, and 20 parts of aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, is dissolved in 200 parts of water. The two solutions are mixed together with agitation, and a precipitate is formed which is sodium aluminum silicate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2$. The precipitate is filtered, washed with water and dried at 105°C . to 110°C . After it is dry, the sodium aluminum silicate is ground in the presence of water in a ball mill until it is reduced to a fine powder.

A stereotype dry mat is then prepared containing the sodium aluminum silicate which has been described as the filler by a procedure which is similar to that customarily used in preparing stereotype dry mats and which has been described in a general way in the foregoing. In accordance with such procedure an aqueous slurry of alpha cellulose fibers is placed in a beater and beaten until the fibers are well separated and have undergone a suitable amount of hydration. An aqueous suspension of the sodium aluminum silicate is then added to the slurry and the mass is agitated in the beater until the fibers and particles of sodium aluminum silicate are thoroughly mixed together, the proportions in this mass being 100 parts of fibers and 23 parts of sodium aluminum silicate. The mass is transferred to a paper-making wet machine and the amounts of water and solids are adjusted to provide a suspension of the desired concentration. The mixture of fibers and discrete particles of sodium aluminum silicate is then felted into the form of a thin web upon the screen of the machine, the web is transferred to a moving felt and then to a roll upon which it is wound until a sufficient number of layers have accumulated to form a sheet of the desired thickness. The wet sheet is then transferred to a dryer where it is dried and at the same time calendered upon its face. A release-promoting coating such as has been described in the foregoing is applied to the face of the mat. The stereotype dry mat contains approximately 13.6 percent of sodium aluminum silicate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2$.

The stereotype dry mat so formed is ready for use, and for molding purposes is moistened with 25 percent of moisture, based on the weight of the moistened mat. It is then subjected to molding and casting in accordance with the procedure described hereinbefore. The mat of this example was so molded and cast, and was found to take a deep and clear-cut impression from the printing form and to produce a cast metal plate which is an excellent reproduction of the printing form. In the moistened condition the mat is characterized by a high degree

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of plasticity such that it takes a deep and well-defined impression from the printing form and has a smooth surface which is free of minute roughness and projecting fibers. The impression taken by the mat is clear-cut in the finest details, including the halftones. After the molding operation, the moisture is readily released in the scorching operation so that the mat is quickly and completely freed of moisture. During drying the mat shrinks uniformly throughout its area. The dried mat is flexible so that it readily conforms to the curved shape of the casting box. The mat is strong and its face is tough and resistant to the heat of the molten metal and is smooth and free from projecting fibers, whereby the cast plates are readily released without impairment of the casting surface of the mat. As a result, a relatively large number of casts of high quality are obtained from a single mat, which is the desideratum of stereotyping procedure.

Several additional sodium aluminum silicates were formed by the procedure described in the foregoing, using sodium silicates of different ratios from $1\text{Na}_2\text{O}:\text{SiO}_2$ to $1\text{Na}_2\text{O}:3.75\text{SiO}_2$. Also, sodium aluminum silicates were formed by a procedure generally similar to that described in the foregoing and substituting sodium aluminate, NaAlO_2 for aluminum sulfate in the reaction with sodium silicate. Stereotype mats were made containing such sodium aluminum silicates as fillers, and such mats were subjected to molding and casting procedure and found to give excellent results.

Example 2

Sodium zinc silicate is prepared by reacting 45 parts of sodium silicate having the ratio $1\text{Na}_2\text{O}:2\text{SiO}_2$ with 20 parts of zinc sulfate, ZnSO_4 , in aqueous solution, and then filtering, washing, drying and grinding the resulting sodium zinc silicate in a procedure similar to that described in connection with Example 1. A stereotype dry mat was prepared containing discrete particles of the sodium zinc silicate as filler, and the resulting mat was molded and cast in a procedure similar to that described in connection with Example 1, and the mat was found to exhibit high plasticity when moist and satisfactory molding and casting properties.

In the same way, double silicates of sodium and amphoteric metals other than aluminum and zinc were prepared by procedures similar to that described in connection with Example 1 as follows: sodium lead silicate by reacting 45 parts of sodium silicate with 67 parts of lead acetate, $\text{Pb}(\text{CH}_3\text{COO})_2$; sodium tin silicate by reacting 45 parts of sodium silicate with 33 parts of stannous chloride, SnCl_2 ; sodium tin silicate by reacting 45 parts of sodium silicate with 53 parts of sodium stannate, Na_2SnO_3 ; sodium iron silicate by reacting 45 parts of sodium silicate with 20 parts of ferric chloride, FeCl_3 ; sodium chromium silicate by reacting 45 parts of sodium silicate with 35 parts of chromic nitrate, $\text{Cr}(\text{NO}_3)_3$; sodium chromium silicate by reacting 45 parts of sodium silicate with 65 parts of sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$; sodium titanium silicate by reacting 45 parts of sodium silicate with 6.5 parts of titanium trichloride, TiCl_3 ; sodium manganese silicate by reacting 45 parts of sodium silicate with 25 parts of manganous chloride, MnCl_2 ; sodium molybdenum silicate by reacting 36 parts of sodium silicate with 26 parts of sodium molybdate, Na_2MoO_4 .

Stereotype dry mats were prepared containing, respectively, each of the double silicates of sodium and amphoteric metal set forth in the foregoing by a procedure similar to that described in connection with Example 1, and such mats were found to exhibit satisfactory molding and casting properties.

In a similar manner, potassium aluminum silicates were formed by reacting potassium silicate with aluminum sulfate in aqueous solution, and stereotype dry mats were prepared containing the potassium aluminum

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silicates as filler and were found to exhibit excellent plasticity when moist and improved molding and casting properties.

Zeolites which are commercially available upon the market are also suitable for use as filler in a stereotype dry mat in accordance with the present invention. Such zeolites which have been used with satisfactory results are the following, designated by trade name or trademark: "Culligan," "Decalso," "Aridzone" and "Zeolox 23." These zeolites are all sodium aluminum silicates and have been found to give excellent results when used as filler in a stereotype dry mat. An additional zeolite which has been found to be satisfactory for the purpose of the invention is that described in United States Patent No. 1,949,360.

The cation exchange products of the synthetic inorganic gel zeolites described in the foregoing are also suitable for use as fillers in stereotype dry mats in accordance with the present invention. By "cation exchange products," when that term is used in the specification and claims, is meant those products formed by passing in contact with the zeolite water containing dissolved therein a cation other than the cation contained by the zeolite. For example, an aqueous solution of calcium chloride was passed in contact with the "Culligan" sodium aluminum silicate zeolite in which operation the sodium of the zeolite was replaced with calcium, with the formation of a calcium aluminum silicate zeolite. In a similar manner, aqueous solutions of magnesium chloride, ammonium chloride and guanidine carbonate were passed in contact with the same sodium aluminum silicate zeolite with the formation of magnesium aluminum silicate, ammonium aluminum silicate and guanidine aluminum silicate. Stereotype mats containing, respectively, each of these compositions were prepared and subjected to molding and casting operations as described in the foregoing and were found to exhibit superior plasticity when moist and to possess the other desirable properties which have been described in the foregoing.

The property of cation exchange which has been described is not essential to the successful use of the synthetic inorganic gel zeolites as fillers in accordance with the present invention, and it is not known that all of such zeolites described herein possess the property of cation exchange, and the term "cation exchange products," as used herein in the specification and claims, contemplates those products which are formed by cation exchange with the synthetic inorganic zeolites which possess the property of cation exchange. Similarly, while the term "zeolite" is commonly applied to substances possessing the property of cation exchange, for the reason pointed out in the immediate foregoing, this term, as used herein in the specification and claims, is not restricted to compositions possessing the property of cation exchange, but designates generically the compositions having the structure of the synthetic gel double silicates which have been described, regardless of whether they possess cation exchange properties.

To show the comparative molding plasticity exhibited by stereotype dry mats containing as filler a synthetic inorganic gel zeolite in accordance with the present invention and stereotype mats containing an ordinary filler such as clay, depths of impression measurements were made upon metal plates which had been made by casting against such mats. The mat with the zeolite filler contained 13.6 percent of the commercially available sodium aluminum silicate sold under the trademark "Zeolox 23," and the other mat contained 13.7 percent of clay as the filler. These proportions are on a weight basis, the proportions of filler being given in terms of the amount of filler, exclusive of water of hydration, based on the combined weight of the filler and the fibers, exclusive of moisture. Both of the mats were subjected to identical molding procedure. They were first moistened to a moisture content of 25 percent, based on the weight of

the moistened mat. They were molded by means of the same printing form, and the form was pressed against the mat with the same pressure, namely, 2,000 pounds per square inch. A metal plate was cast from each of the molded mats. The depth of impression was measured by means of a depthometer made by Allan B. Croke Company, and measurements were taken at the same locations upon the metal plate cast from each of the mats. At three locations, at letters in the printing, the depths of impression in the mat containing "Zeolex 23" were, respectively, .0075 inch, .0095 inch and .0080 inch, and at the corresponding locations in the mat containing clay the depths were .0050 inch, .0070 inch and .0060 inch. At one location in the highlight screen of the illustration (where shading is almost white), the depth in the mat containing "Zeolex 23" was .0055 inch, and the depth in the mat containing clay was .0040 inch. At one location in the middle tone screen of the same illustration (where shading is medium gray), the depth of impression in the mat containing "Zeolex 23" was .0040 inch, and the depth in the mat containing clay was .0035 inch. The depth of impression was, at every location, substantially greater in the mat containing "Zeolex 23" than in the mat containing clay.

In a stereotype dry mat, the shrinkage during drying after molding is effected by the amounts of moisture and filler in the mat. The mat of the invention provides the advantage that shrinkage can be effected in the desired manner by regulating the amount of filler while at the same time the desired strength of the mat is retained.

In the procedure described in the foregoing for preparing the synthetic inorganic gel zeolite, the product formed by reacting the soluble silicate with the soluble amphoteric metal compound is filtered, washed, dried and ground before it is mixed with the fibers. It is not essential that it be washed, and the entire reaction mass may be dried and then ground in the ball mill, because when the resulting powder is mixed with the fibers the soluble constituents are substantially dissolved and eliminated in the waste water of the wet machine.

In the foregoing description, including the examples, a stereotype dry mat is described as containing a single synthetic inorganic zeolite as the filler, and it is to be understood that mixtures of such fillers, and mixtures of such zeolite fillers with other fillers may be used if desired. In the descriptions of the examples, the stereotype dry mat is stated as being composed of alpha cellulose fibers, and it is to be understood that other kinds of fibers may be used as is stated in the earlier portion of the description. Other changes and variations may be made as will occur to those skilled in the art.

Invention is claimed as follows:

1. A stereotype dry mat comprising a co-felted mixture of cellulose fibers and discrete particles of a filler, said filler containing as an essential ingredient a substance selected from the group consisting of pre-formed synthetic inorganic gel zeolites and the cation exchange products thereof, said zeolites comprising double silicates of an alkali metal selected from the group consisting of sodium and potassium, and an amphoteric metal, the amount of said zeolite, exclusive of water of hydration, being between about 1% and about 50% of the combined dry weight of the fibers and the oxide, said stereotype dry

mat being characterized by high plasticity when moist, whereby said mat is capable of taking an impressing from a printing form.

2. A stereotype dry mat according to claim 1 wherein said alkali metal is sodium and said amphoteric metal is aluminum.

3. A stereotype dry mat according to claim 1 wherein said alkali metal is potassium and said amphoteric metal is aluminum.

4. A stereotype dry mat according to claim 1 wherein said amphoteric metal is lead.

5. A stereotype dry mat according to claim 1 wherein said amphoteric metal is zinc.

6. A stereotype dry mat according to claim 1 wherein said amphoteric metal is iron.

7. A stereotype dry mat according to claim 1 wherein said amphoteric metal is titanium.

8. A stereotype dry mat comprising a co-felted mixture of cellulose fibers and discrete particles of a filler and having a water content of approximately 7% to 50% based on the weight of the total of said mat and water, said filler containing as an essential ingredient a substance selected from the group consisting of pre-formed synthetic inorganic gel zeolites and the cation exchange products thereof, said zeolites comprising double silicates of an alkali metal selected from the group consisting of sodium and potassium, and an amphoteric metal the amount of said zeolite, exclusive of water of hydration, being between about 1% and about 50% of the combined dry weight of the fibers and the oxide, said stereotype dry mat being characterized by high plasticity when moist, whereby said mat is capable of taking an impression from a printing form.

9. A stereotype dry mat comprising a co-felted mixture of cellulose fibers and discrete particles of a filler, said filler containing as an essential ingredient a substance selected from the group consisting of pre-formed synthetic inorganic gel zeolites and the cation exchange products thereof, said zeolites comprising double silicates of an alkali metal selected from the group consisting of sodium and potassium, and an amphoteric metal, the amount of said substance being approximately 1% to 50% based on the dry weight of said mats, said stereotype dry mat being characterized by high plasticity when moist, whereby said mat is capable of taking an impression from a printing form.

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