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(54) **Titre : PRODUITS D'ENCOLLAGE ET DE RHEOLOGIE AMELIORES POUR SYSTEMES A BASE DE GYPSE ET DE STUC
 DESTINES A LA PRODUCTION DE PANNEAUX RESISTANT A L'EAU**
 (54) **Title: IMPROVED SIZING AND RHEOLOGY AGENTS FOR GYPSUM STUCCO SYSTEMS FOR WATER RESISTANT PANEL
 PRODUCTION**

(57) **Abrégé/Abstract:**

Emulsions, and processes for making the emulsions, useful for imparting water resistance to gypsum products are disclosed. Process for making the emulsion and gypsum products made from the emulsion are also disclosed. The emulsions of the invention include at least one paraffin wax and a hydrophilic metallic salt. The emulsions of the invention may further include a saponifiable wax substitute for montan wax. The emulsions of the invention may further include a biocide.



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(54) Title: IMPROVED SIZING AND RHEOLOGY AGENTS FOR GYPSUM STUCCO SYSTEMS FOR WATER RESISTANT PANEL PRODUCTION

(57) Abstract: Emulsions, and processes for making the emulsions, useful for imparting water resistance to gypsum products are disclosed. Process for making the emulsion and gypsum products made from the emulsion are also disclosed. The emulsions of the invention include at least one paraffin wax and a hydrophilic metallic salt. The emulsions of the invention may further include a saponifiable wax substitute for montan wax. The emulsions of the invention may further include a biocide.



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**IMPROVED SIZING AND RHEOLOGY AGENTS FOR GYPSUM STUCCO
SYSTEMS FOR WATER RESISTANT PANEL PRODUCTION**

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10 **FIELD OF THE INVENTION**

[0002] The present invention relates to wax emulsions useful in imparting water resistance to gypsum products. In addition the present invention relates to methods of preparing the wax emulsions and to articles prepared there-from.

15 **BACKGROUND OF THE INVENTION**

[0003] Certain properties of gypsum (calcium sulfate dihydrate) make it very popular for use in making industrial and building products; especially gypsum board. It is a plentiful and generally inexpensive raw material which, through a process of dehydration and rehydration, can be cast, molded or otherwise formed to useful shapes. The base material from which gypsum board is manufactured is the hemihydrate form of calcium sulfate (gypsum), commonly termed stucco, which is produced by the heat conversion of the dihydrate from which the water phase has been removed.

[0004] The manufacture of gypsum products generally includes preparing a gypsum-containing slurry that contains gypsum and other components of the finished product, and then processing the slurry to remove the water and form and dry the remaining solids into the desired form. In one example of the making of a gypsum board, the gypsum slurry must flow onto a paper substrate. In a continuous process, the slurry/substrate combination is then sized by passing this combination between rollers. Simultaneous with this sizing step, a paper backing is positioned over the sized gypsum slurry. Accordingly, the gypsum slurry must possess sufficient fluidity so that a properly sized gypsum board can be made. Fluidity refers to the ability of the gypsum slurry to flow.

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[0005] One undesirable trait of gypsum is that gypsum absorbs water, which reduces the strength of the products in which it is used and enables deleterious biological activity, such as the growth of mildew, mold, and other undesirable organism, to occur therein and thereon. Prior art products, like ordinary gypsum board, gypsum tile, gypsum
5 block, gypsum casts, and the like have relatively little resistance to water. When ordinary gypsum board, for example, is immersed in water, the board quickly absorbs a considerable amount of water, and loses a great deal of its strength. Actual tests have demonstrated that when a 2 inch by 4 inch cylinder of gypsum board core material was immersed in water at about 70°F (21.1 C°), the cylinder showed a water absorption of
10 36% after immersion for 40 minutes.

[0006] Previous attempts to provide water-resistant properties to gypsum board include incorporation of asphalt, metallic soaps, resins, and wax additives into a aqueous gypsum slurry. The resulting materials were difficult to use and the core properties
15 difficult to control. Polysiloxane-based systems have also been used in attempts to impart water-resistance to gypsum board. However, the polysiloxane-based systems are both expensive and difficult to use. Polyvinyl alcohol has been used in an attempt to provide a room temperature system for use in adding water resistant properties to gypsum. However, the polyvinyl alcohol system tends to rapidly separate and thus typically requires
20 continuous mixing prior to use, and there is also the potential for bacterial growth.

[0007] A finished gypsum product has also been coated with water resistant films or coatings. One specific example of a past attempt to provide a water-resistant gypsum product is the spraying of a molten paraffin wax or asphalt into an aqueous gypsum slurry.
25 However, these coating applications add additional process complexity and machinery complexity to the manufacturing process as well as extending production times.

[0008] Additionally, existing products used to make wax emulsions for gypsum boards are available in less than sufficient amounts. For example, montan wax, made
30 from lignite coal, is an existing product for use in wax emulsions for gypsum. However, montan wax is made only by a few manufacturers, and supplies and deliveries of materials have been observed to be insufficient for modern manufacturing process.

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[0009] Accordingly, there is a need for a wax emulsion which is useful in imparting water-resistance to gypsum products, and which is economical to apply. There is a need for alternative components for wax emulsions useful in imparting water-resistance to gypsum products. There also remains a need for an additive which is useful in imparting resistance to biological growth on gypsum products, and which is economical to employ.

SUMMARY OF THE INVENTION

[0010] Embodiments of the invention are directed to wax emulsions for providing water-resistance to a gypsum product. The wax emulsions include at least one paraffin wax and a hydrophilic metallic salt.

[0011] In one aspect of the invention, an emulsion is provided for providing water-resistance to a gypsum product, including at least one paraffin wax, wherein each paraffin wax of the at least one paraffin wax, comprises a melting point from about 57°C and about 66°C, an oil content from about 0.1% to less than 1% by weight of the wax, a flash point from about 200°C to about 240°C, and an average carbon number of the paraffin from 29 to 32, a hydrophilic metallic salt, and water. In another aspect of the invention, the invention includes gypsum products prepared utilizing the emulsion of the invention.

[0012] In another aspect of the invention, a method is provided for making the emulsion for providing water-resistance to a gypsum product, including providing a first mixture comprising at least one paraffin wax and a saponifiable wax, wherein each paraffin wax of the at least one paraffin wax comprises a melting point between about 57°C and about 66°C, an oil content from about 0.1% to less than 1% by weight of the wax, a flash point from about 200°C to about 240°C, and an average carbon number of the paraffin from 29 to 32, and wherein the saponifiable wax comprises a solidification temperature from about 60°C to about 90°C, a saponification value from about 30 to about 120, and an acid value from about 10 to about 40, providing a second mixture comprising a hydrophilic metallic salt and water, combining the first mixture and the second mixture to form a resultant mixture, and homogenizing the resultant mixture.

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[0012a] In accordance with one aspect of the present invention, there is provided an emulsion for providing water-resistance to a gypsum product, comprising: at least one paraffin wax, wherein each paraffin wax of the at least one paraffin wax, comprises a melting point from about 57°C and to about 66°C, an oil content from about 0.1% to less than 1% by weight of the wax, a flash point from about 200°C to about 240°C, and an average carbon number of the paraffin from 29 to 32; a saponifiable wax, wherein the saponifiable wax comprises a solidification temperature from about 60°C to about 90°C, a saponification value from about 30 to about 120, and an acid value from about 10 to about 40; a hydrophilic metallic salt comprising a compound selected from the group consisting of magnesium sulfate, potassium sulfate, lithium sulfate, ammonium sulfate, potassium acetate, ammonium heptamolybdate, and combinations thereof; and water.

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[0013] In another aspect of the invention, an emulsion is provided for providing water-resistance to a gypsum product, including at least one paraffin wax, wherein each paraffin wax of the at least one paraffin wax, comprises a melting point from about 57°C and about 66°C, an oil content from about 0.1% to less than 1% by weight of the wax, a flash point from about 200°C to about 240°C, and an average carbon number of the paraffin from 29 to 32, a saponifiable wax, wherein the saponifiable wax comprises a solidification temperature from about 60°C to about 90°C, a saponification value from about 30 to about 120, and an acid value from about 10 to about 40, a hydrophilic metallic salt, and water. In another aspect of the invention, the invention includes gypsum products prepared utilizing the emulsion of the invention.

[0014] In another aspect of the invention, a method is provided for making the emulsion for providing water-resistance to a gypsum product, including providing a first mixture comprising at least one paraffin wax and a saponifiable wax, wherein each paraffin wax of the at least one paraffin wax comprises a melting point between about 57°C and about 66°C, an oil content from about 0.1% to less than 1% by weight of the wax, a flash point from about 200°C to about 240°C, and an average carbon number of the paraffin from 29 to 32, and wherein the saponifiable wax comprises a solidification temperature from about 60°C to about 90°C, a saponification value from about 30 to about 120, and an acid value from about 10 to about 40, providing a second mixture comprising a hydrophilic metallic salt and water, combining the first mixture and the second mixture to form a resultant mixture, and homogenizing the resultant mixture.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The present invention provides wax emulsions that are useful in imparting water-resistance properties to gypsum products. In addition, the wax emulsions may be used in the manufacture of additional products, such as gypsum products having wood fiber or other lignocellulosic materials. The wax emulsions include at least one paraffin wax and a hydrophilic metallic salt. The wax emulsion may be free of an alkyl phenol, free of a starch component, or both. The wax emulsions of the present invention may be added to mixtures of gypsum and water without adversely affecting properties of the

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mixture which are necessary to the manufacture of gypsum products such as gypsum board.

[0016] Waxes useful in the emulsions of the invention include paraffin waxes having desired physical properties. The paraffin waxes may have a melting point from about 57°C (135°F) to about 66°C (151°F). The paraffin waxes may have an minimum flash point of 200°C or greater, such as from about 200°C (392°F) to about 245°C (473°F), such as from about 204°C (399°F) to about 243°C (470°F). Also, the oil content of the paraffin waxes may be less than about 1% by weight, such as from about 0.1% to less than 1 wt%, for example from about 0.4 wt% to less than about 0.7% by weight. The paraffin waxes may have an average chain length of about 29 to 32 carbon atoms (C₂₉-C₃₂). The paraffin waxes are typically of low volatility, exhibiting less than about a 10% loss in weight during standard thermogravimetric analysis. The paraffin waxes may be non-saponifiable waxes.

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[0017] Examples, of suitable paraffin waxes include a wax selected from the group of Exxon ParvanTM 1370, Exxon ParvanTM 1380, Exxon ParvanTM 1420, Exxon ParvanTM 1451, IGI 1301A, IGI 1302A, IGI 1304A, Nippon SerioTM 145, and combinations thereof. Exxon ParvanTM 1370, Exxon ParvanTM 1380, Exxon ParvanTM 1420, Exxon ParvanTM 1451 are commercially available from Exxon-Mobil, Inc., of Bayton, Texas. IGI 1301A, IGI 1302A, and IGI 1304A, are commercially available from International Group Incorporated, of Farmers Valley, Pennsylvania. Nippon SerioTM 145 is commercially available from Nippon Serio, of Tokuyama, Japan. Sample properties for the suitable paraffin wax examples are shown in Table 1 below.

25

Table 1

Waxes	Melt Temp °C (°F)	Oil Content	Flash Temp °C (°F)	Average Carbon number Total Paraffins
Exxon Parvan TM 1370	57.0°C (135°F)	0.1% to 0.7%	> 204°C (400°F)	29

Exxon Parvan TM 1380	57.8°C (136°F)	0.1% to 0.6%	> 204°C (400°F)	29
Exxon Parvan TM 1420	60.0°C (140°F)	0.1% to 0.6%	> 210°C (410°F)	31
Exxon Parvan TM 1451	61.1°C (142°F)	0.1% to 0.5%	> 210°C (410°F)	31
IGI 1301A	61.7°C (143°F)	0.1% to 0.5%	>243°C (470)	30/32
IGI 1302A	60.0°C (140°F)	0.1% to 0.5%	> 238°C (460°F)	30/32
IGI 1304A	65.6°C (150°F)	0.1% to 0.7%	> 236°C (460°F)	30/32
Nippon Serio TM 145	61.3°C (143°F)	0.1% to 0.4%	> 238°C (460°F)	31

[0018] In certain embodiments, it is useful to saponify one or more of waxes for use in the emulsion. In this way, a saponified wax functions as an added surfactant or dispersant.

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[0019] In one embodiment, a saponifiable wax is added the emulsion. Saponifiable waxes useful in this respect are limited to waxes having an acid value or a saponification value and a melting point greater than about 180°F (82.2°C). Waxes which may be saponified in the emulsions of the present invention include montan wax, carnauba wax, beeswax, bayberry-myrtle wax, candelilla wax, caranday wax, castor bean wax, esparto grass wax, Japan wax, ouricury wax, retamo-ceri mimibi wax, shellac, spermaceti wax, sugar cane wax, wool-lanolin wax, and combinations thereof, among others. Montan wax is made from lignite or brown coal.

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[0020] Saponification of such waxes may be accomplished by combining the wax with a strongly basic material such as an alkali metal hydroxide or other hydroxide. Examples of such hydroxides include sodium hydroxide, potassium hydroxide, ammonium hydroxide, and combinations thereof. The amount of strongly basic material needed to saponify a wax may be calculated based on the saponification value of the wax. For example, the saponification value divided by 1000 equals the grams of potassium hydroxide to add per gram of wax.

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[0021] Alternatively, a saponifiable wax substitute for montan wax (also referred to as a montan wax substitute) may be used for the saponifiable wax. The saponifiable wax substitute for montan wax may comprise a petroleum derived wax base material, such as paraffin wax, microcrystalline wax, or both. The saponifiable wax substitute for montan wax may further include one or more organically derived waxes, a carboxylic acid, other organic components, such as triglycerides and ketones, among others. For example, the saponifiable wax substitute for montan wax may comprise a microcrystalline wax derived from petroleum, a caruba wax, and stearic acid. The saponifiable wax substitute for montan wax may be free of a montan wax. The emulsion may be free of a montan wax. In one embodiment, a montan substitute wax and a montan wax and/or other saponifiable wax as described herein may be used in combination for the emulsion. In such an embodiment, the montan wax and/or other saponifiable wax as described herein may be used in an amount comprising about 5% or less, such as from 0.1% to 5 %, by weight of the emulsion.

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[0022] The saponifiable wax substitutes for montan wax may have a saponification value from about 30 to about 120, such as from about 45 to about 105. The saponifiable wax substitutes for montan wax may have an acid number of from about 10 to about 40, such as from about 12 to about 36. Suitable saponifiable wax substitutes for montan wax include waxes having a combined acid number and saponification value in the combined range from about 40 to about 160, such as from about 50 to about 140, for example, from about 55 to about 120. The saponifiable wax substitutes for montan wax may have a solidification temperature from about 60°C to about 90°C, such as from about 65°C to about 85°C.

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[0023] Examples of suitable saponifiable wax substitutes for montan wax include 2432 MontanTM Wax Substitute, 2437 MontanTM Wax Substitute, 2438 MontanTM Wax Substitute, and combinations thereof. 2432 MontanTM Wax Substitute, 2437 MontanTM Wax Substitute, and 2438 MontanTM Wax Substitute, are commercially available from The British Wax Refining Co., Ltd., of The United Kingdom. The properties for the above waxes are shown in Table 2 below. Other waxes believed to be suitable for use in the emulsion include 2431 MontanTM Wax Substitute and 2436 MontanTM Wax Substitute, and which waxes

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may be used in combination or as substitutes for the 2432 MontanTM Wax Substitute, 2437 MontanTM Wax Substitute and 2438 MontanTM Wax Substitute described herein. 2431 MontanTM Wax Substitute and 2436 MontanTM Wax Substitute are commercially available from The British Wax Refining Co., Ltd., of The United Kingdom.

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Table 2

Waxes	Solidification Temp °C ASTM D938	Acid Value ASTM D1386	Saponification Value ASTM D1387
2432 Montan TM Wax Substitute	65-72°C	12-25	45-60
2437 Montan TM Wax Substitute	78-84°C	15-35	80-105
2438 Montan TM Wax Substitute	78-84°C	15-35	80-105
2431 Montan TM Wax Substitute	75-80°C	22-36	75-100
2436 Montan TM Wax Substitute	78-84°C	15-25	80-105

[0024] Typical composition ranges for the emulsion of the invention useful in providing water-resistance to a gypsum product include any combination of the following. The at least one paraffin wax may be present in the emulsion in an amount of about 25% to about 40% by weight based on the total weight of the emulsion. A saponifiable wax may be present in an amount of about 2.5% to about 4.5% by weight based on the total weight of the emulsion. Water may be present in an amount of about 55% to about 65% by weight based on the total weight of the emulsion to form the emulsion.

[0025] The emulsions may also include a hydrophilic metallic salt, such as magnesium sulfate (MgSO₄). Suitable hydrophilic metallic salts include magnesium sulfate, potassium sulfate, lithium sulfate, ammonium sulfate, potassium acetate, ammonium heptamolybdate, and combinations thereof. The hydrophilic metallic salt, such as magnesium sulfate (MgSO₄), may be present in the emulsion in an amount of about 0.05% to about 5% by weight, such as about 0.05% to about 3.0%, for example,

from about 0.1% to about 2.5%, and in a further example, between about 0.1 % to about 1.0%, based on the total weight of the emulsion.

[0026] It is believed that the hydrophilic metallic salt eliminates the use of starch
5 as a suspension/gelation aid, and to be compatible with a wider range of available waxes
(i.e. lower cost/lower melt point waxes). Examples of the starches utilized as a
suspension/gelation aid are described in US Patent Application Publication No.
2005/0250858 A1 and in US Patent No. 6,663,707.

Thus, the emulsion may be free of a starch component.

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[0027] Additionally, hydrophilic metallic salts, such as $MgSO_4$, are believed to be
water soluble and offer an opportunity to disperse wax, suspended as an emulsion, more
uniformly through a stucco/core substrate, and to be compatible with a wider range and
lower cost/lower melt point of available waxes. The $MgSO_4$ containing emulsion of the
15 present invention also allows a reduction in the use of the alkylated phenol, which
functioned as a dispersant in the historic system. As a result the wax emulsion of the
present invention is significantly more stable than former or competitive systems and may
be stored at higher solids content, with out comprising the performance or stability of the
emulsion. The emulsion may be free of alkyl phenols. As used herein, "alkyl phenols"
20 refer to phenolic compounds having a long chain alkyl group.

[0028] Additional components including an ionic dispersant, an alkali metal
hydroxide, and combinations thereof, may also be used with the waxes in the emulsions
described herein.

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[0029] The ionic dispersant may include cationic materials, such as cationic
surfactants. The ionic dispersant may include a compound selected from the group of
polynaphthalenesulfonic acid, a lignosulfonate, and combinations thereof. The ionic
dispersant may be used in an amount of about 0.25% to about 5.0% by weight based on
30 the total weight of the emulsion. An example of a polynaphthalenesulfonic acid ionic
dispersant is DISAL™ surfactant from Handy Chemicals Limited Corporation of Canada.

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An example of a lignosulfonate ionic dispersant is POLYFON™ H surfactant commercially available from MeadWestvaco Corporation of Richmond, Virginia.

[0030] In embodiments of the emulsion utilizing a saponifiable wax substitute for montan wax, the ionic dispersants may be selected from the group of a polynaphthalenesulfonic acid, a lignosulfonate, a polynaphthalene sulfonate calcium salt, and combinations thereof. The ionic dispersants may be used in an amount of about 0.25% to about 5.0% by weight based on the total weight of the emulsion. In one embodiment, the ionic dispersant comprises a mixture of a polynaphthalenesulfonic acid, a lignosulfonate, and polynaphthalene sulfonate calcium salt, and the ionic dispersant mixture comprises from about 0.25% to about 5.0% by weight based on the total weight of the emulsion. Examples of polynaphthalene sulfonate calcium salt ionic dispersants are Durasar surfactant and Gypserse surfactant from Handy Chemicals Limited Corporation of Canada.

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[0031] The alkali metal hydroxide may be used in an amount or about 0.2% to about 1.5% by weight based on the total weight of the emulsion. The alkali metal hydroxide may be added in an aqueous solution, for example about 45 wt% potassium hydroxide solution. The alkali metal hydroxide may be selected from the group consisting of potassium hydroxide, sodium hydroxide, and combinations thereof. Additionally, ammonium hydroxide may be used separately, or in combination with the alkali metal hydroxide, in the emulsion.

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[0032] An optional component for the emulsions or gypsum formulations described herein includes a biocide, which may also be referred to as a preservative. The biocides disclosed herein are useful for inhibiting biological growth, for example, the growth of mildew, fungi, bacteria, algae, and other microorganisms, on gypsum products. As used herein biocides includes such compounds as bactericides, fungicides, algacides, mildewcides, or a combination thereof.

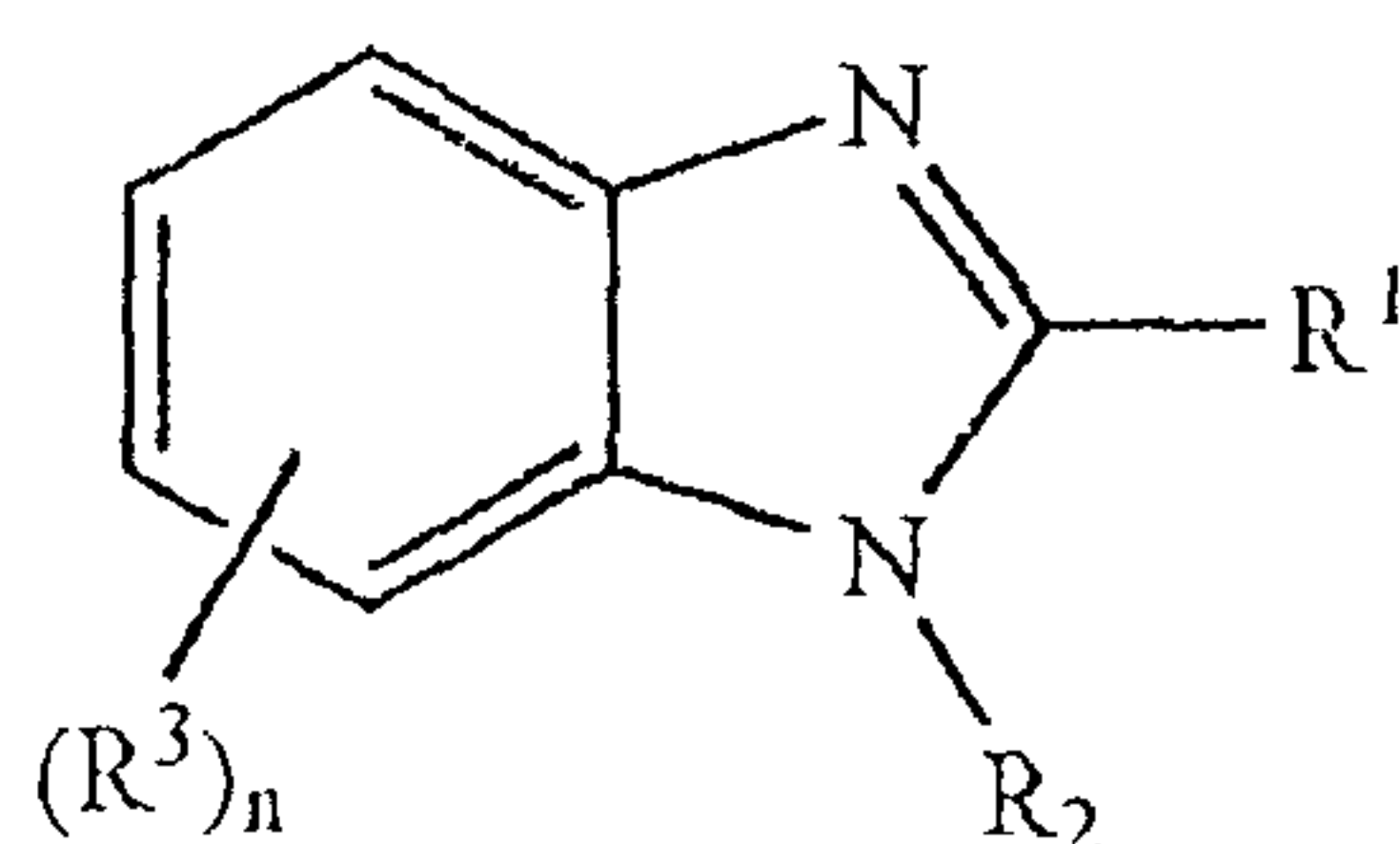
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[0033] The biocide may be chosen according to (1) the target organism; (2) solubility characteristics; (3) stability to the temperature and pH; and other conditions

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found in the manufacture of the gypsum product. Biocides include substances that kill or inhibit the growth of microorganisms such as molds, mildew, slimes, fungi, bacteria, etc. Fungicides include substances that kill or inhibit the growth of fungi. More specific examples of biocides include, but are not limited to, chlorinated hydrocarbons, organometallics, halogen-releasing compounds, metallic salts, organic sulfur compounds, and phenolics. Preferred biocides have the general structure of a heterocycle containing nitrogen and sulfur, for example, thiabendazole [2-(4-thiazolyl)-1H-benzimidazole].

[0034] Exemplary biocides (preservatives) include the compositions disclosed in U.S. Pat. No. 3,370,957 to *Wagner et al.*, and U.S. Pat. No. 7,294,189 to *Wantling* and which discloses biocides according to the general structure (I):



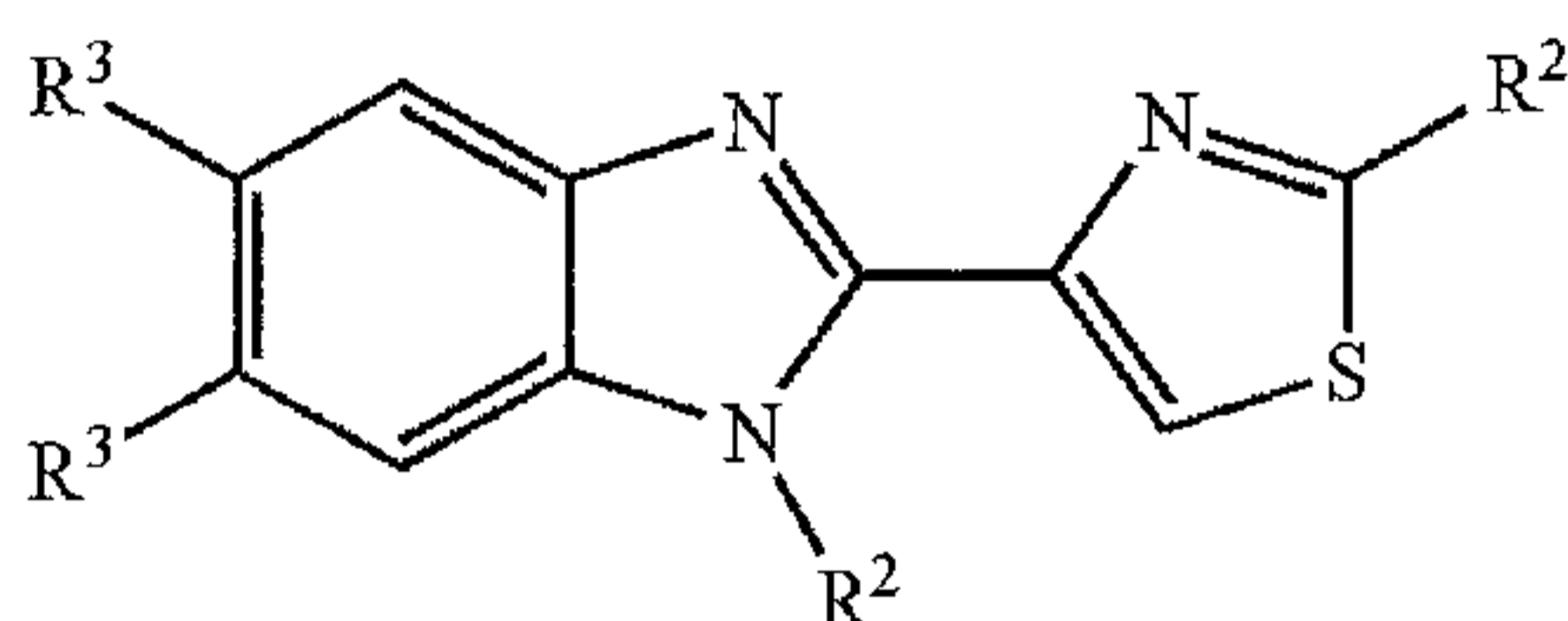
[0035] wherein R^1 can be a heterocycle containing nitrogen and sulfur, such as thiazolyl, isothiazolyl, or thiadiazolyl, which can optionally be substituted with C_1 - C_6 alkyl; R^2 can be hydrogen or C_1 - C_6 alkyl, specifically hydrogen; n is 0, 1, 2, or 3; each instance of R^3 can independently be hydrogen, C_1 - C_6 alkyl, phenoxy, C_1 - C_6 alkoxy, halo, amino, C_1 - C_6 alkylamino, di C_1 - C_6 alkyl amino, imidazolyl, thiazolyl, isothiazolyl, thiadiazolyl, thienyl, furyl, pyrrol, naphthyl, phenyl, halophenyl, C_1 - C_6 alkyl phenyl, C_1 - C_6 alkoxyphenyl, and the like.

[0036] Particular embodiments of the mildewcide include those according to the general structures (II) and (III):

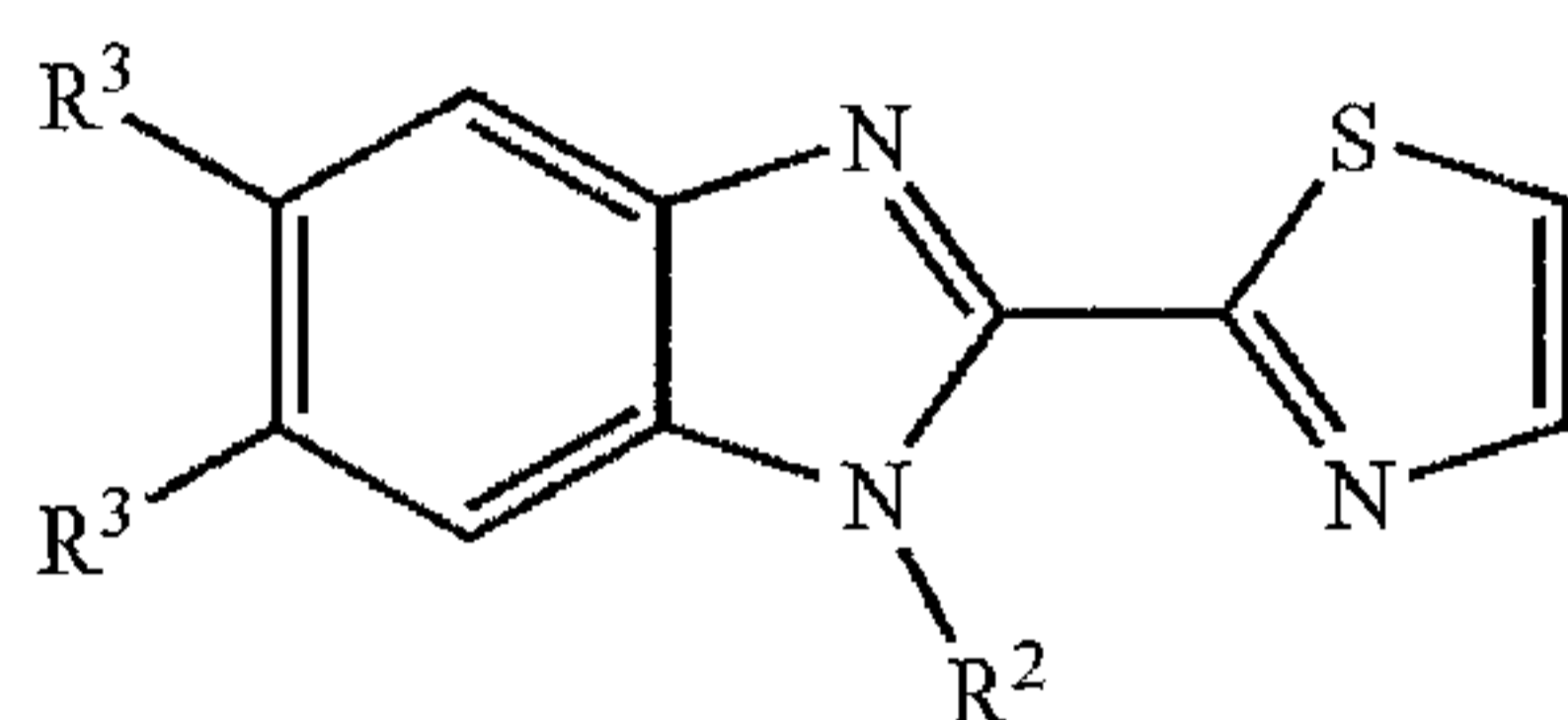
25

(II)

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(III)



[0037] wherein R¹, R², and R³ are as defined previously.

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[0038] Exemplary mildewcides according to structure (I) include: 2-(4'-thiazolyl) benzimidazole; 2-[3'-(1',2',5'-thiadiazolyl)] benzimidazole; 2-(4'-thiazolyl)-5-methoxy benzimidazole; 2-(4'-thiazolyl)-5-phenoxy benzimidazole hydrochloride; 2-(2'-methyl-4'-thiazolyl) benzimidazole; 2-[4'-(1',2',3'-thiadiazolyl)] benzimidazole; 1-acetyl-2-(4'-thiazolyl)-5-phenyl benzimidazole; 2-(4'-isothiazolyl) benzimidazole; 2-(4'-thiazolyl)-6-fluoro benzimidazole; 2-(4'-thiazolyl)-5-amino benzimidazole; 2-(2'-thiazolyl)-5-(1'-imidazolyl) benzimidazole; 2-(4'-isothiazolyl)-5-chlorobenzimidazole; 2-(4'-thiazolyl)-5-phenyl benzimidazole; 2-[4'-(1',2',3'-thiadiazolyl)]-5-(4'-tolyl) benzimidazole; 1-acetyl-2-(2'-thiazolyl)-5-phenyl benzimidazole; 1-methyl-2-(2'-isothiazolyl)-5-(2'-methoxyphenyl) benzimidazole; 2-(4'-isothiazolyl)-5-furyl benzimidazole; 2-(4'-thiazolyl)-5-(4'-fluorophenyl) benzimidazole hydrochloride; 2-(4'-thiazolyl)-5-bromo benzimidazole; 2-(4'-thiazolyl)-5-chloro benzimidazole; 2-(2'-thiazolyl)-5-methoxy benzimidazole; 2-(4'-thiazolyl)-5-(2'-fluorophenyl) benzimidazole hydrochloride; 2-[3'-(1',2',5'-thiadiazolyl)] 1-5-methylthio benzimidazole; 2-(4'-thiazolyl)-5,6-difluoro benzimidazole; 1-benzoyl-2-(4'-thiazolyl) benzimidazole; 2-(2'-thiazolyl)-5-(2'-pyrryl) benzimidazole; 1-methyl-2-(4'-isothiazolyl) benzimidazole hydrochloride; 2-(4'-thiazolyl)-5-phenoxy benzimidazole; 2-[3'-(1',2', 5'-thiadiazolyl)]1-5-methoxy benzimidazole; 1-ethyl-2-(4'-thiazolyl)-5-(2'-

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thiazolyl) benzimidazole; 1-acetyl-2-[3'-(1',2',5'-thiadiazolyl)]-5-(2"-furyl) benzimidazole; 2-(4'-thiazolyl)-4-fluoro benzimidazole hydrochloride; 2-(2'-thiazolyl) benzimidazole; 1-acetyl-2-(4'-thiazolyl) benzimidazole; and combinations thereof. In a particular embodiment described below, thiabendazole (2-(4'-thiazolyl) benzimidazole) has been
5 found to be effective in inhibiting the growth of biological agents on gypsum board, thus indicating the advantageous utility of benzimidazole compounds generally and the other biocides indicated herein.

[0039] In one embodiment, the biocide is added as the last ingredient in the wax emulsion, for example, the biocide is added to the already-formed wax emulsion. The
10 biocide may be present in the wax emulsion in an amount of 0.01 to 10% by weight of the wax emulsion (wt. %), optionally 0.1 to 5 wt. %, for example, 0.2 to 4 wt. %. The biocide may be added in any convenient form, including 100% solids, as a hydrated paste or in a water diluted system, for example, 25-50% active thiabendazole. The biocide is preferably
15 added with agitation, which is believed to thoroughly disperse the biocide into the discontinuous wax phase of the emulsion. Optionally, one or more of the biocides may be employed in an amount calculated to be about 0.0025% to about 0.2% by weight of the finished gypsum product. The biocide is post-added to the wax emulsion under severe agitation to any desired wax emulsion where the water phase is the continuous phase in
20 amounts ranging from 0.01 to 5% (percent) by volume.

[0040] The wax emulsions of the present invention have been observed to have desirable properties. The emulsions of the present invention have been observed to be stable for at least one (1) week, such as for at least one (1) month, and for example, for at least 6
25 months. The wax emulsion formed herein also exhibited the properties as follows. The wax emulsions have a pH of less than 12, such as from about 10.5 to about 12, for example, from about 10.9 to about 11.1. The wax emulsions may have a viscosity from about 1 cps to about 30 cps, such as from about 2 cps to about 14 cps.

[0041] Additionally, the typical mean solids content of the emulsions of the invention have been observed to be at least 30% by weight, preferably at least 40% by weight, more preferably at least 50%, and even more preferably at least 60% by weight.
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In one embodiment, the solids may be present from about 33% to about 42% by weight of the emulsion. Stability of the higher solids content emulsions are beneficial in the potential to reduce transportation costs.

5 [0042] The resulting wax emulsion can be used in the preparation of gypsum products and does not have significant affect on the desired properties of the finished products, such properties including strength, facing bonds, and water resistance where applicable. Various sources of gypsum may be used in the compositions of the present invention. However, the amount of water required to hydrate a gypsum sample will vary
10 with the purity of the sample. The wax emulsions may be added to mixtures of gypsum and water without adversely affecting properties of the mixture which are necessary to the manufacture of gypsum products such as gypsum board and GWF. Such properties include fluidity, formability and set time. In the manufacture of gypsum wallboard products it is important to impart water resistance to the finished product, so as to limit the maximum
15 water absorption realized by the wallboard in a defined board soak test. For example, American Standards for Testing Materials ASTM 1396 and sub parts thereof describe such a test.

[0043] The wax emulsions produced gypsum materials having a water absorption
20 from about 0.1% to about 3%, such as from about 0.15% to about 2.8%. The wax emulsions produced gypsum materials having a fluidity/rheology from about 2.75 inches in patty diameter to about 3.5 inches in patty diameter, such as from about 2.9 inches in patty diameter to about 3.4 inches in patty diameter under the test as described herein.

25 [0044] In the manufacture of conventional gypsum board, the wax emulsion enters the process and is introduced into the stucco (gypsum) slurry at a mixer just prior to being released into a forming station for the board. In the case of gypsum wood fiber process, the emulsion is introduced into the fourdiner section of a paper machine. In one embodiment, the emulsion comprises from about 1 wt% to about 7 wt.%, such as from
30 about 1.5 wt% to about 3 wt.%, of the combined emulsion and gypsum composition. In another embodiment, the emulsion is added in sufficient quantity to provide from 1 wt.%

to about 5 wt.%, such as from about 1.5 wt% to about 3 wt.%, of wax solids into the gypsum and emulsion composition.

[0045] The gypsum board may comprise at least gypsum, the at least one paraffin wax, the saponifiable wax, and the hydrophilic metallic salt as described above, and optionally water. The gypsum may further include additional materials, such as lignocellulosic materials, such as wood or wood fibers. The gypsum board may further include any additional emulsion components described herein, such as the biocide described herein.

10

[0046] The wax emulsions containing the components described herein may also be added to the resin used in making various kinds of panel boards that do not contain gypsum. For example, emulsions described herein are useful in improving the water resistance of lignocellulosic products, thus ameliorating the detrimental effects that absorbed water can have on such products, including dimensional instability (swelling) and biological degradation as described in the process and materials of US Patent No. 7,807,735.

15

[0047] In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered.

20

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145								
Montan	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
MgSO ₄	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DISAL ²	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Polyfon H ³	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
45% aq. KOH	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Water	60.75	60.75	60.75	60.75	60.75	60.75	60.75	60.75
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<u>Emulsion Properties</u>								
pH	10.99	11.01	10.95	11.02	11.01	10.92	10.96	10.99
Solids	37.78	38.7	33.63	41.06	38.28	33.82	34.69	38.42
Viscosity Cps	8	5.7	2.8	9.8	13.3	3.2	4.7	7.8
<u>Results of Gypsum Formulations</u>								
Patty diameter (inches)	2.95	3.08	3.33	3.16	2.94	3.29	3.18	3.24
Water Absorption	0.87	0.19	0.74	0.88	2.79	1.02	1.5	1.96

¹ All component and solid values are % by wt.² DISAL™ is a polynaphthalenesulfonic acid dispersant available from Handy Chemical, Montreal, Quebec, Canada.³ POLYFON™ H is a lignosulfonate dispersant available from MeadWestvaco Corporation, Stamford, Connecticut

- 5 [0050] Table 3-1 includes fluidity and absorption data obtained for test specimens prepared utilizing the emulsions. All gypsum formulation test specimens were made by mixing 50 grams of stucco (the hemihydrate form of calcium sulfate) with water and the emulsion together and allowed to stand for one minute. The mixing amounts for the above emulsions are shown in Table 3-2 below.

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Table 3-2

Emulsion	Stucco (grams)	Water Amount (grams)	Emulsion Amount (grams)
1	50	32.5	4
2	50	32.6	3.9
3	50	32	4.45
4	50	32.85	3.65
5	50	32.6	3.9
6	50	32.1	4.45
7	50	32.2	4.33
8	50	32.6	3.9

5 [0051] This mixture was then mixed for an additional 30 seconds. After this second mixing, the specimens were poured out onto a flat surface and the diameter of the resulting patty was measured. The diameter of a patty is an index of the fluidity of the specimen. The larger the diameter, the more fluid the specimen. Patties made in the fluidity test were dried for at least 24 hours at 110°F (43.3 °C). At the end of this time, the
10 patties were weighed and the weight was recorded.

[0052] The dried patties were then immersed in water for two hours. At the end of the two hour immersion, the patties were weighed and this wet weight was recorded. The percent water retention was then calculated based on the difference between these two
15 recorded weights.

[0053] While not being held to any particular theory, it is believed that the oil content relates to effectiveness of the formation of the emulsion and the resulting gypsum formulations. High oil contents, i.e., greater than 2% detrimentally affect the performance
20 and physical properties of those waxes used to form emulsions. Additionally, waxes

without oil content are also believed to detrimentally affect the performance and physical properties of those waxes used to form emulsions.

[0054] In contrast, waxes not suitable for use in gypsum wax formulations were also observed. The not suitable wax (ineffective formulations) emulsions were prepared and tested as described above for the Table 3-1 emulsions and with the components and results listed in the following Tables 4 and 5.

Table 4

10

Waxes	Melt Temp °C (°F)	Oil Content (wt.%)	Flash Temp °C (°F)	Average Carbon number Total Paraffins
Sunwax 20	40-55°C (104-131°F)	15-20%	> 204°C (399°F)	22-26
Exxon Prowax TM 561	64.0°C (147°F)	15-20%	> 232°C (450°F)	32
Exxon Parvan TM 1380	57°C (135°F)	15-20%	> 280°C (425°F)	28
Exxon Prowax TM 390	68°C (154.4°F)	3-5.0%	> 232°C (450°F)	22/24
Alpha-Olefin 30+	72.2°C (162°F)	0	> 252°C (485°F)	30
Alpha-Olefin 30+	67.8°C (154°F)	0	>222°C (432)	30
Alpha-Olefin 30+	35.6°C (96°F)	0	> 183°C (362°F)	20-24
Alpha-Olefin 30+	66.1°C (151°F)	0	> 218°C (425°F)	24-28

Table 5¹

Component	1	2	3	4	5	6	7	8
Sunwax TM 20	33.5	--	--	--	--	--	--	--
Exxon Prowax TM	--	33.5	--	--	--	--	--	--

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561								
S-Wax TM	--	--	33.5	--	--	--	--	--
Exxon Prowax TM 390	--	--	--	33.5	--	--	--	--
Alpha-Olefin C30	--	--	--	--	33.5	--	--	--
Alpha-Olefin C30HA	--	--	--	--	--	33.5	--	--
Alpha-Olefin C20-24	--	--	--	--	--	--	33.5	--
Alpha-Olefin C24-28	--	--	--	--	--	--	--	33.5
Montan	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
MgSO ₄	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
DISAL ²	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Polyfon H ³	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
45% aq. KOH	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Water	60.75	60.75	60.75	60.75	60.75	60.75	60.75	60.75
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
<u>Emulsion Properties</u>								
pH	10.97	11.01	10.95	11.02	11.01	10.92	10.96	10.99
Solids	32.53	38.7	33.63	41.06	38.28	33.82	34.69	38.42
Viscosity Cps	3.1	5.7	2.8	9.8	13.3	3.2	4.7	7.8
<u>Results of Gypsum Formulations</u>								
Patty diameter (inches)	--	--	--	--	--	--	--	--
Water Absorption	--	--	--	--	--	--	--	--

¹ All component and solid values are % by wt.² DISALTM is a polynaphthalenesulfonic acid dispersant available from Handy Chemical, Montreal, Quebec, Canada.³ POLYFONTM H is a lignosulfonate dispersant available from MeadWestvaco Corporation, Stamford, Connecticut

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[0055] As shown above, only selected paraffin waxes, the recited paraffin waxes with desired properties with examples shown in Table 3-2, would produce wax emulsions suitable for forming gypsum formulations suitable for industrial use. The other emulsion, which have a paraffin wax with at least one physical property outside of the recited paraffin wax property description, failed to produce suitable wax emulsion and gypsum formulations as shown in Tables 4 and 5. The emulsions 1-8 shown in Table 5 each had a mixture that thickened too much to pour a patty for testing when mixed with gypsum, and the data is represented as "--" for no result. The gypsum formulation products for emulsions 1-8 in Table 5 also could not be tested for water absorption as no patties could be formed as detailed above, and thus, the data is represented as "--" for no result.

[0056] In a further example, additionally tests were performed for the saponifiable wax substitutes for montan wax as described herein for Table 3-1 wax emulsions, and the results are presented in the following Table 6-1. Nippon Serio 145 for the table below may also be referred to as Luxco G-Wax, which is commercially available from Luxco of Richmond, California.

Table 6-1¹

Component	1	2	3	4
Nippon Serio TM 145	33.5	33.5	33.5	33.5
German Montan TM	33.5	--	--	--
2432 Montan TM Wax Substitute	--	33.5	--	--
2437 Montan TM Wax Substitute	--	--	33.5	--
2438 Montan TM Wax Substitute	--	--	--	33.5
MgSO ₄	0.5	0.5	0.5	0.5
DISAL ²	0.55	0.55	0.55	0.55
Polyfon H ³	0.5	0.5	0.5	0.5

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Durasar ⁴	0.6	0.6	0.6	0.6
45% aq. KOH	0.65	0.65	0.65	0.65
Water	60.2	60.2	60.2	60.2
Total	100.00	100.00	100.00	100.00
<u>Emulsion Properties</u>				
pH	--	10.33	10.26	10.33
Solids	--	38.59	38.46	38.36
Viscosity cps	--	8.3	7.1	9.6
<u>Results of Gypsum Formulations</u>				
Patty diameter (inches)	--	2.7	3.39	3.4
Water Absorption	--	1.06	2.09	0.78

¹ All component and solid values are % by wt.

² DISAL™ is a polynaphthalenesulfonic acid dispersant available from Handy Chemical, Montreal, Quebec, Canada.

³ POLYFON™ H is a lignosulfonate dispersant available from MeadWestvaco Corporation, Stamford, Connecticut

⁴ Durasar is a polynaphthalene sulfonate calcium salt surfactant available from Handy Chemical, Montreal, Quebec, Canada.

5

[0057] The mixing amounts for the gypsum formulations of the above emulsions are shown in Table 6-2 below.

Table 6-2

10

Stucco (grams)	Water Amount (grams)	Emulsion Amount(grams)	Emulsion
50	35	0	1 (Control)
50	32.6	3.9	2
50	32.6	3.9	3
50	32.6	3.9	4

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[0058] Table 6-1 and 6-2 show that the saponifiable wax substitutes for montan wax provide effective patty formulation as compared to montan wax alone, which failed to form a gypsum formulation that could be tested.

5 [0059] While the present invention has been described and illustrated by reference to particular embodiments and examples, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

CLAIMS:

1. An emulsion for providing water-resistance to a gypsum product, comprising:

at least one paraffin wax, wherein each paraffin wax of the at least one paraffin wax, comprises a melting point from about 57°C and to about 66°C, an oil content from about 0.1% to less than 1% by weight of the wax, a flash point from about 200°C to about 240°C, and an average carbon number of the paraffin from 29 to 32;

a saponifiable wax, wherein the saponifiable wax comprises a solidification temperature from about 60°C to about 90°C, a saponification value from about 30 to about 120, and an acid value from about 10 to about 40;

a hydrophilic metallic salt comprising a compound selected from the group consisting of magnesium sulfate, potassium sulfate, lithium sulfate, ammonium sulfate, potassium acetate, ammonium heptamolybdate, and combinations thereof; and

water.

2. The emulsion of claim 1, further comprising one or more components selected from the group consisting of an ionic dispersant, an alkali metal hydroxide, and combinations thereof.

3. The emulsion of claim 1 or 2, wherein the at least one paraffin wax is in an amount of about 25% to about 40% by weight based on the total weight of the emulsion, and the saponifiable wax is in an amount of about 2.5% to about 4.5% by weight, based on the total weight of the emulsion.

4. The emulsion of any one of claims 1 to 3, wherein the hydrophilic metallic salt is present in an amount of about 0.05% to about 5% by weight, based on the total weight of the emulsion.

5. The emulsion of any one of claims 1 to 4, wherein the hydrophilic metallic salt comprises a magnesium sulfate.
6. The emulsion of claim 2, wherein the ionic dispersant comprises a mixture of a polynaphthalenesulfonic acid, a lignosulfonate, and polynaphthalene sulfonate calcium salt, and the ionic dispersant mixture comprises from about 0.25% to about 5.0% by weight based on the total weight of the emulsion.
7. The emulsion of claim 2, wherein the alkali metal hydroxide comprises from about 0.5% to about 1.5% by weight, based on the total weight of the emulsion.
8. The emulsion of any one of claims 1 to 7, wherein the water comprises from about 55% to about 65% by weight based on the total weight of the emulsion.
9. The emulsion of any one of claims 1 to 8, wherein the emulsion comprises a solids content of at least 30% by weight, based on the total weight of the emulsion.
10. The emulsion of any one of claims 1 to 9, further comprising a biocide.
11. The emulsion of claim 10, wherein the biocide comprises a heterocycle compound containing nitrogen and sulfur.
12. The emulsion of claim 11, wherein the heterocycle compound comprises thiabendazole (2-(4-thiazolyl)-1H-benzimidazole).
13. A gypsum product comprising gypsum and the emulsion of any one of claims 1 to 12.
14. The gypsum product of claim 13, wherein the hydrophilic metallic salt comprises magnesium sulfate is in an amount of about 0.05% to about 5% by weight, based on the total weight of the emulsion.

15. A method for making an emulsion according to any one of claims 1 to 12, comprising the steps of:

providing a first mixture comprising at least one paraffin wax and a saponifiable wax, wherein each paraffin wax of the at least one paraffin wax comprises a melting point between about 57°C to about 66°C, an oil content from about 0.1% to less than 1% by weight of the wax, a flash point from about 200°C to about 240°C, and an average carbon number of the paraffin from 29 to 32, and wherein the saponifiable wax comprises a solidification temperature from about 60°C to about 90°C, a saponification value from about 30 to about 120, and an acid value from about 10 to about 40;

providing a second mixture comprising a hydrophilic metallic salt and water;

combining the first mixture and the second mixture to form a resultant mixture; and

homogenizing the resultant mixture.