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⑰ **Use of alkylamine salts as viscosity regulating substance.**

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CHEMICAL ABSTRACTS, vol. 22, no. 4, Feb 1928; P.WALDEN et al.: "Investigations on low-melting salts. I. Preparation and densities of low-melting picrates", p. 520

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Description

Technical field

The present invention relates to the use of acid addition salts of alkyl amines for regulating the viscosity of paper coating mixes when blending such mixes.

The object of the present invention is to enable the interchange of coating mixes in continuous paper coating processes without substantial change in the viscosity of said mixes at the transition from one mix to the other and/or the mixing of the mixes one with the other.

Background of the invention

Paper is coated by applying an extremely thin layer of coating mix to a paper web. The purpose of the coating is to improve the properties of the paper, particularly with regard to uniformity of surface, and its ability to accept inks, lacquers etc. from the printing press. Such mixes today comprise finely ground kaolin, dispersant, and water, or chalk, dispersant, water. Mixes have also been proposed, and prepared that comprises calcium sulphate dihydrate (gypsum), dispersant and water. It has also been found, however, that when switching from a gypsum mix to a kaolin mix the viscosity of the combined mixes is much higher than that of a single mix, which renders the system inoperable.

Due to the complexity of paper machines it is not convenient to stop production in order to clean the coating equipment. It is also necessary, however, to be able to switch from one type of mix to another without stopping production in order to satisfy demands for paper with different coatings.

Various systems have been tested, inter alia with variation of the dispersant, although without success.

DE—A1—1 696 193 discloses the use of polyvinylalcohol as a binding agent in satin white-based coating mixtures, whereby an amine, alkali or ammoniumsalt of a polycarboxylic acid is used as an impart useable viscosity to the formulation. The polycarboxylic acids used are particularly those being of high molecular weight, such as sodium polyacrylate, sodium polyvinyl sulphonate, and sodium carboxy methyl cellulose.

EP—A2—0 004 062 discloses aqueous dispersions of polymers, particularly on the basis of vinylpolymers, whereby salts of primary, secondary and tertiary aliphatic amines are used as dispersing agents.

Summary of the invention

It has now surprisingly been found possible to solve this problem in a simple and efficient manner by means of the present invention which to this end proposes the use of compounds which comprise an acid addition salt of an alkyl amine having 1—5 carbon atoms in the alkyl chain, preferably 2—4 carbon atoms and still more preferably 3—4 carbon atoms.

Part of the alkyl amine is present as an acid addition salt. The acid addition salt is prepared by reaction with sulphuric acid, phosphoric acid, hydrochloric acid, nitric acid, perchloric acid, aliphatic, alicyclic, aromatic and heterocyclic carboxylic and sulphonic acids. In this regard, such salts are hydrochlorides, sulphate, hydrogen sulphate, phosphate, hydrogen phosphate, nitrate, formiate, acetate, propionate, succinate, glycolate, gluconate, heptonate, lactate, tartrate, citrate, oxalate, ascorbate, maleate, hydroxy maleate, benzoate, p-amino benzoate, p-hydroxy benzoate, salicylate, p-amino salicylate, picrate, diethylene triamine pentaacetate (DTPA), ethylene diamine tetraacetate (EDTA), nitrilo triacetate (NTA), hydroxy ethyl imino diacetate, bis(hydroxyethyl)gluconate.

Further characteristics are set forth in the following claims.

The alkyl amines used in the group preferably comprise primary alkyl amines, such as methyl amine, ethyl amine, propyl amine, 1-methyl ethyl amine, butyl amine, 1-methyl propyl amine, 2-methyl propyl amine, pentyl amine, 3-methyl butyl amine, 2-methyl butyl amine, 1-ethyl propyl amine, 1-methyl butyl amine, 1,1-dimethyl ethyl amine, 1,1-dimethyl propyl amine, although they may also comprise secondary, tertiary and quarternary alkyl amines, such as dimethyl amine, diethyl amine, triethyl amine, tetramethyl amine.

The product is prepared by mixing a solution of an alkyl amine with a solution of an acid which will react to form the intended acid addition salt. It is irrelevant in this respect whether one solution is added to the other, or vice versa.

The respective solutions may have the form of a concentrate or a solvent solution of the compound concerned.

The ratio of amine to acid is from 1 to 4, depending upon the degree of substitution desired.

In the process of adding one solution to the other, care is taken to ensure that the alkyl amine does not boil, by a suitable control of temperature.

The reaction between alkyl amine and acid takes place instantaneously, whereafter the product can be filtered off (when the reaction takes place in a non-dissolving solvent) or can be used direct, in solution.

Example 1

33.6 kg of citric monohydrate were dissolved in 30 l of water. 36 l (25.9 kg) of n-propyl amine were then added carefully to the solution, while stirring and cooling the system. The temperature was maintained beneath 45°C. The resultant product, (n-propylamine)₃-citrate remained in solution in the water phase.

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The following systems were prepared in a similar manner:

		Melting point °C
5	2. (sec.butyl amine) ₂ -sulphate	>250
	3. (sec.butyl amine) ₂ -hydrogen phosphate	130—195
	4. (sec.butyl amine) ₁ -acetate	
	5. (sec.butyl amine) ₂ -citrate	
	6. (n-butyl amine) ₂ -sulphate	
10	7. (n-propyl amine) ₂ -sulphate	
	8. (isobutyl amine) ₂ -sulphate	
	9. (methyl amine) ₂ -sulphate	
	10. (tert.butyl amine) ₂ -sulphate	
	11. (sec.butyl amine) ₃ -phosphate	
15	12. (n-butyl amine) ₃ -phosphate	
	13. (isobutyl amine) ₃ -phosphate	
	14. (tert.butyl amine) ₃ -phosphate	
	15. (n-propyl amine) ₃ -phosphate	
	16. (n-propyl amine) ₂ -hydrogen phosphate	
20	17. (n-propyl amine) ₂ -citrate	
	18. (n-propyl amine) ₃ -citrate	
	19. (sec.butyl amine) ₂ -oxalate	
	20. (sec.butyl amine) ₄ -EDTA:te	
25	A1. (n-octyl amine) ₂ -sulphate	>250 decomp. 220°C

A1 is a compound used in comparative testing.

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A series of experiments was conducted on the basis of the above substances, in which there was prepared a first kaolin mix comprising 100 parts of dry kaolin, 50 parts of water, 0.35 parts of 100%-Dispex[®] and NaOH. The pH of the mix was 8.5. A suspension was then prepared over a period of one hour, by adding to the mix 9 parts of DOW 685, 1.2 parts of CMC (carboxy methyl cellulose) and water to a viscosity of about 1500 cps, dry solids (DS) content 55—58%. Peripheral data concerning different starting kaolin mixes is given in Table 1 below, left column.

A further gypsum based mix was prepared from 100 parts dry gypsum, 1.5 parts CMC, 9 parts latex DOW 685, NaOH to pH 8.5 and water, there being obtained a mix with DS 64.4%, viscosity 950 cps. Various amines according to the foregoing were added to 400 g of the kaolin mix thus prepared, in the quantities set forth in Table 1, whereafter 30.1 g of the gypsum mix were added and the viscosity of the resultant mixture was measured. The viscosity was also measured after adding the amine. The results obtained when adding the gypsum based mix are set forth in the right column of Table 1 below.

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TABLE 1

	Amine No.	Viscosity before	Amine amount % charged	DS before %	pH	Viscosity after	DS after %	pH
5	—	1460	—	58.3	8.6	7300	58.6	7.6
	2	1440	0.1	58.3	8.4	2440		7.6
10	2	1600	0.2	58.3	8.1	2200		7.6
	2	1640	0.5	58.3	7.8	1840		7.5
	2	1640	1.0	58.3	7.6	1760		7.5
	3	1440	0.04	58.5	8.4	2280	58.6	7.6
	3	1460	0.2		8.1	1760		7.5
15	3	1680	0.5		7.8	2040		7.5
	3	1800	1.0		7.6	2320		7.4
	19	1600	0.2		7.3	1840		6.6
	19	1840	0.5		6.2	2000		5.8
	19	2340	1.0		5.2	3300		4.9
20	19	1400	0.05		8.1	3680		7.3
	—	1340	—	57.3	8.3	6200	57.6	7.5
	6	1360	0.2		7.9	1780		7.4
	6	1480	0.5		7.6	1620		7.3
	6	1680	1.0		7.4	1700		7.3
25	8	1360	0.2		7.9	1740		7.4
	8	1460	0.5		7.7	1580		7.3
	8	1580	1.0		7.5	1600		7.3
	10	1440	0.2		8.0	1820		7.4
	10	1380	0.5		7.7	1520		7.3
30	10	1440	1.0		7.4	1540		7.2
	5	1240	0.2		6.4	1540		5.9
	5	1200	0.5		5.6	1400		5.1
	5	1480	1.0		5.4	1600		4.9
	7	1340	0.2		7.9	1640		7.4
35	7	1320	0.5		7.7	1540		7.4
	7	1540	1.0		7.6	1660		7.4
	A1	2340	0.2		7.7	>10,000		7.1
	A1	>10,000	0.5		7.4	>10,000		7.0
	A1	impossible	1.0		—	—		—
40	—	1200	—		8.4	6100	58.0	7.6
	12	1240	0.05		8.3	2000		7.5
	12	1440	0.10		8.2	1800		7.5
	12	1520	0.2		8.1	1880		7.5
	12	1600	0.5		8.1	2000		7.6
45	13	1340	0.1		8.2	1940	58.5	7.5
	13	1400	0.2		8.2	1820		7.4
	13	1440	0.5		8.1	1840		7.5
	14	1360	0.1		8.2	1780		7.4
	14	1420	0.2		8.1	1700		7.4
50	14	1520	0.5		7.9	1860		7.4
	11	1420	0.1		8.2	2080		7.5
	11	1500	0.2		8.0	1860		7.6
	11	1540	0.5		7.9	1740		7.6
	3	1280	0.1		8.2	1860		7.6
55	3	1360	0.2		8.1	1800		7.6
	3	1320	0.5	57.3	8.0	1680	58.5	7.5
	15	1380	0.1		8.3	1700		7.5
	15	1420	0.2		8.2	1680		7.5
	15	1380	0.5		8.1	1780		7.6
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The present invention has also been tested on a semi-industrial scale in an apparatus having a volume of 25 litres. The apparatus comprised a machine tank having a volumetric filling capacity of 15 litres, a filter, and a buffer tank provided with an outlet leading to the machine tank and to the "coating station", i.e. the

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apparatus simulated the coating of a paper web by taking out 1 litre of mix per minute. The volume circulated was 7 litres and the flow rate 10 litres per minute. The system was filled with a mix 1. Whereafter the mix was pumped around the system, and "coating commenced". Subsequent to emptying the machine tank, by consecutive simulated "coating" procedures, such that about 10 litres of mix 1 remained, the system was refilled with mix 2, this mix being intended to replace mix 1 without interrupting circulation and while continuing the "coating" process. Samples were taken from the combined mixture of mixes 1 and 2 at 30 second intervals, in order to determine the viscosity, pH, and in some cases also DS and the ratio of mix 1 to mix 2 in the combined coating mixture.

The results set forth in Table 2 were obtained when testing a conventional kaolin coating mix (mix 2), 100 parts of kaolin, 0.35 parts Dispex^R N40, 1.2 parts of CMC FF5, and 9 parts of latex DOW 685, DS 56—59%, pH 8.5—9, and a gypsum-based coating mix (mix 1) comprising 100 parts of dry gypsum dihydrate, 1.5 parts of CMC, and 9 parts of DOW 685, DS 60—65%, pH 8.5—9, without further addition of a compound according to the present invention.

TABLE 2
With no addition

	min.	mix 2	mPas	mix 1, %
0	0	x	1000	100
	1		2600	60
	1.5		3200	
25	2.0		2300	
	2.5		3000	45
	3.0		3300	
	3.5		2500	
	4.0		3000	
30	4.5		2600	
	6.0	x	2100	40
	7.0		3200	30
	7.5		3900	
	8.0		3200	
35	8.5		4100	25
	9.0		3200	
	10.0		3200	
	10.5		4000	
	12	x	1900	
40	12.5		3500	
	13.0		5200	
	14.0		4200	
	15.0		4500	
	15.5		5500	
45	16.0		4200	10
	16.5		3700	

Table 3 below discloses the results obtained when adding to mix 1 (the gypsum mix) 0.4 parts of propyl amine phosphate, calculated as amine.

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TABLE 3
With the addition of 0.4 parts (propyl amine)₃ phosphate

	Time min.	Addition mix 2	Viscosity mPas	Content mix 1, %
5	0	x	900	100
	1		1500	75
	1.5		2000	
10	2		1900	
	3		1900	
	4		1900	
	4.5		1900	25
	6	x	1800	
15	7		1800	
	8		1800	10
	9		1800	
	10		1800	
20	12		1850	
	13		1850	5
	14		1850	
	15		1850	
	16		1850	5

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In a further test, mix 1 and mix 2 were mixed together in different proportions, while carefully stirring the system for one minute. The viscosity of the combined mixture was determined in accordance with the Brookfield technique (30 s 100 rpm). In this test, a study was made of a mixture between a gypsum-based mix according to the above (mix 1) and a kaolin mix (mix 2) with a synthetic thickener, DS 55% and Viscosity mPas. The results are given in Tables 4 and 5 below.

TABLE 4
With no addition

	Mix 1	Mix 2	Viscositet mPas
35	0	100	450
	5	95	2300
40	10	90	2500
	20	80	2000
	40	60	1600
	70	30	1200
	100	0	500

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TABLE 5
With an addition of 0.4 parts (sec.butyl amine)₂ citrate

	Mix 1	Mix 2	Viscosity mPas
50	0	100	450
	5	95	750
	20	80	800
55	40	60	800
	70	30	850
	100	0	500

60 It is evident from the above that the viscosity of the coating mixture is stabilized very effectively when an alkyl amine acid addition salt according to the aforesaid is used.

It has been found that when using the alkyl amine acid addition salt, an acceptable result is achieved even when only a part of the alkyl amine exists in the form of such an acid addition salt.

65 A satisfactory result can also be obtained by adding each of the salt components, i.e. alkyl amine and acid, separately, to the coating mix.

By kaolin-based mix is meant here and in the foregoing, a mix in which the pigment fraction contains more than 50% kaolin. Kaolin mixes that contain 60% kaolin and 40% gypsum are thus known in the art.

By chalk-based mixes is meant a mix that contains more than 50% chalk, while by gypsum-based mixes is meant a mix that contains more than 50% gypsum. Thus the pigment fraction need not be totally based on one pigment.

In the above the abbreviation DS means dry substance; Dow Latex is a polymer, whereby Dow Latex 685 is a carboxylated styrene-butadiene; DISPEX[®] N40 is a sodium salt of polycarboxylic acid; CMC is carboxymethyl cellulose, where CMC FF5 has an extra low viscosity level determined to 35—55 mPa · s at 25°C and a concentration of 4% dry matter.

Claims

1. The use of an acid addition salt of an alkyl amine having 1 to 5 carbon atoms in the alkyl chain for regulating the viscosity of paper coating mixes when blending together different kinds of such mixes, whereby the acid addition salt is a hydrochloride, hydrogen sulphate, hydrogen phosphate, sulphate, phosphate, nitrate, formate, acetate, propionate, succinate, glycolate, heptonate, lactate, tartrate, citrate, oxalate, ascorbate, maleate, hydroxy maleate, benzoate, p-aminobenzoate, p-hydroxy benzoate, salicylate, p-aminosalicylate, picrate, diethylene triamine pentaacetate, ethylene diamine tetraacetate, nitrilo triacetate, hydroxy ethyleneiminodiacetate, and bis-(hydroxyethyl)gluconate.
2. The use according to claim 1, wherein the compound is added in an amount corresponding to 0.05 to 2% by weight of the weight of the ingoing prepared coating mixture.
3. The use according to claim 1, wherein the coating mixtures consist respectively of a kaolin-based and a calcium sulphate-based coating mix.
4. The use according to claim 1, wherein the coating mixes consist respectively of a chalk-based and a calcium sulphate-based coating mix.
5. The use according to claim 1, wherein the coating mixes consist respectively of a kaolin-based and a chalk-based coating mix.
6. The use according to claims 1—5, wherein the alkyl amine has 2 to 4 carbon atoms in the alkyl chain.
7. The use according to claim 6, wherein the alkyl amine has 3 to 4 carbon atoms in the alkyl chain.
8. The use according to claims 1—5, wherein the alkyl amine is a primary alkyl amine.
9. The use according to claims 1—5, wherein the alkyl amine is a secondary alkyl amine.
10. The use according to claims 1—5, wherein the alkyl amine is a tertiary alkyl amine having 1 to 3 carbon atoms in the alkyl groups.
11. The use according to claim 1, wherein the alkyl amine is a quaternary alkyl amine having 1 to 2 C in the alkyl groups.

Patentansprüche

1. Verwendung eines Säureadditionssalzes eines Alkylamins mit 1 bis 5 Kohlenstoffatomen in der Alkylkette zur Regulierung der Viskosität von Papierbeschichtungsgemischen beim Vermischen unterschiedlicher Arten solcher Gemische miteinander, wobei das Säureadditionssalz ein Hydrochlorid, Hydrogensulfat, Hydrogenphosphat, Sulfat, Phosphat, Nitrat, Formiat, Acetat, Propionat, Succinat, Glycolat, Heptonat, Lactat, Tartrat, Citrat, Oxalat, Ascorbat, Maleat, Hydroxymaleat, Benzoat, p-Aminobenzoat, p-Hydroxybenzoat, Salicylat, p-Aminosalicylat, Picrat, Diethylentriaminpentaacetat, Ethylen-diamintetraacetat, Nitrilotriacetat, Hydroxyethyleniminodiacetat und Bis-(hydroxyethyl)-gluconat ist.
2. Verwendung nach Anspruch 1, bei der die Verbindung in einer Menge entsprechend 0,05 bis 2 Gew.-% des Gewichtes des eingehenden hergestellten Beschichtungsgemisches zugesetzt wird.
3. Verwendung nach Anspruch 1, bei der die Beschichtungsgemische jeweils aus einem Beschichtungsgemisch auf Kaolingrundlage und auf Calciumsulfatgrundlage bestehen.
4. Verwendung nach Anspruch 1, bei der die Beschichtungsgemische jeweils aus einem Beschichtungsgemisch auf Kalkgrundlage und auf Calciumsulfatgrundlage bestehen.
5. Verwendung nach Anspruch 1, bei der die Beschichtungsgemische jeweils aus einem Beschichtungsgemisch auf Kaolingrundlage und auf Kalkgrundlage bestehen.
6. Verwendung nach Anspruch 1 bis 5, bei der das Alkylamin 2 bis 4 Kohlenstoffatome in der Alkylkette hat.
7. Verwendung nach Anspruch 6, bei der das Alkylamin 3 bis 4 Kohlenstoffatome in der Alkylkette hat.
8. Verwendung nach Anspruch 1 bis 5, bei der das Alkylamin ein primäres Alkylamin ist.
9. Verwendung nach Anspruch 1 bis 5, bei der das Alkylamin ein sekundäres Alkylamin ist.
10. Verwendung nach Anspruch 1 bis 5, bei der das Alkylamin ein tertiäres Alkylamin mit 1 bis 3 Kohlenstoffatomen in den Alkylgruppen ist.
11. Verwendung nach Anspruch 1, bei der das Alkylamin ein quaternäres Alkylamin mit 1 bis 2 Kohlenstoffatomen in den Alkylgruppen ist.

Revendications

1. Utilisation d'un sel d'addition d'acide d'une alkylamine comportant 1 à 5 atomes de carbone dans la chaîne alkylque pour le réglage de la viscosité de mélanges de couchage du papier lorsqu'on combine ensemble différents types de ces mélanges, le sel d'addition d'acide étant un chlorhydrate, un sulfate monoacide, un phosphate monoacide, un sulfate, un phosphate, un nitrate, un formiate, un acétate, un propionate, un succinate, un glycolate, un heptonate, un lactate, un tartrate, un citrate, un oxalate, un ascorbate, un maléate, un hydroxymaléate, un benzoate, un p-aminobenzoate, un p-hydroxybenzoate, un salicylate, un p-aminosalicylate, un picrate, un diéthylène triamine pentaacétate, un éthylène diamine tétraacétate, un nitrilotriacétate, un hydroxyéthylèneiminodiacétate et un bis(hydroxyéthyl)gluconate.
2. Utilisation suivant la revendication 1, dans laquelle le composé est ajouté en une quantité correspondant à 0,05 à 2% en poids du poids du mélange de couchage préparé entrant.
3. Utilisation suivant la revendication 1, caractérisée en ce que les mélanges de couchage consistent respectivement en un mélange de couchage à base de kaolin et en un mélange de couchage à base de sulfate de calcium.
4. Utilisation suivant la revendication 1, caractérisée en ce que les mélanges de couchage consistent respectivement en un mélange à base de craie et en un mélange à base de sulfate de calcium.
5. Utilisation suivant la revendication 1, caractérisée en ce que les mélanges de couchage consistent respectivement en un mélange à base de kaolin et en un mélange à base de craie.
6. Utilisation suivant l'une quelconque des revendications 1 à 5, caractérisée en ce que l'alkylamine comporte 2 à 4 atomes de carbone dans la chaîne alkyle.
7. Utilisation suivant la revendication 6, caractérisée en ce que l'alkylamine comporte 3 ou 4 atomes de carbone dans la chaîne alkyle.
8. Utilisation suivant l'une quelconque des revendications 1 à 5, dans laquelle l'alkylamine est une alkylamine primaire.
9. Utilisation suivant l'une quelconque des revendications 1 à 5, caractérisée en ce que l'alkylamine est une alkylamine secondaire.
10. Utilisation suivant l'une quelconque des revendications 1 à 5, caractérisée en ce que l'alkylamine est une alkylamine tertiaire comportant de 1 à 3, atomes de carbone dans le groupe alkyle.
11. Utilisation suivant la revendication 1, caractérisée en ce que l'alkylamine est une alkylamine quaternaire comportant 1 ou 2 atomes de carbone dans le groupe alkyle.