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METHOD OF PURIFYING WATERS

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The present invention relates to a method of conditioning an aqueous bath having ingredients present inducing foaming of the bath, said method comprising introducing into the bath a mixture of saturated and unsaturated amines of high molecular weight and containing at least 11 carbon atoms in an alkyl radical thereof, said amines being characterized by the properties of being insolvent in the bath and showing little tendency to saponify with the ingredients of the bath, the amines being present in amounts sufficient to inhibit foaming of the bath.

The present invention is admirably adapted for the conditioning of boiler waters and particularly those having excess alkalinity.

In one form of the invention the aqueous bath may be treated with a secondary or tertiary aliphatic amine.

The invention, in its narrower form, contemplates the treatment of waters with saturated and/or unsaturated aliphatic amines, their substitution products and/or derivatives, said compounds containing eleven (11) or more carbon atoms, being substantially insoluble in water, and showing little tendency to steam distill. In the more specific form of the invention, said compounds are used to inhibit the foaming tendency of raw or softened alkaline waters and particularly boiler waters having excess alkalinity, or an alkalinity present in a quantity more than sufficient to combine with or existing in combination with the calcium and/or magnesium ions, calcium or magnesium salts or their equivalents contained in the water.

It may be stated that the solubility of the aliphatic amines, their substitution products and/or derivatives in water decrease with the molecular weight thereof, and, therefore, in accordance with the present invention, it is preferred to use those amine compounds which have high molecular weight, and by this is meant compounds having eleven (11) carbon atoms or more, and typified by undecyl amine, dodecyl amine, tridecyl amine, and the like, these all being straight chain primary amines.

As previously pointed out, aliphatic amines which are sparingly soluble, or substantially insoluble, may be used as the primary anti-foam agent in a composition adapted to inhibit the foaming in waters containing ingredients inducing foaming therein. These amines, their substitution products and derivatives, are particularly capable of giving satisfactory results in inhibiting the foaming tendency of waters containing excess alkalinity, and particularly excess sodium and potassium alkalinity. These amines as a group show substantially no tendency to saponify in the water or aqueous bath treated. Preferably, where the water treated is subjected to a high temperature, the aliphatic amines

should not steam distill to any material extent. Examples of aliphatic amines which may be used in accordance with the present invention are hexadecyl amine ($C_{16}H_{33}NH_2$), heptadecyl amine ($C_{17}H_{35}NH_2$) and octadecyl amine ($C_{18}H_{37}NH_2$).

It may be pointed out that in accordance with the present invention, it is the intention to use the broad class of amines, either aliphatic or aromatic, which are sparingly soluble, or substantially insoluble in water, and which prevent the foaming of the water or the aqueous bath treated. Generally, it is the amines of high molecular weight which are the most satisfactory, and as a general rule, it may be stated that the most insoluble ones are the amines which contain more than ten (10) carbon atoms, particularly the straight chain primary amines. However, it may be pointed out that the split chain primary amines, as well as the straight chain and split chain secondary and tertiary amines, may be used in accordance with the present invention.

Other straight chain primary amines which may be used as an anti-foam agent are:

- 25 Undecyl amine ($C_{11}H_{23}NH_2$)
- Dodecyl amine ($C_{12}H_{25}NH_2$)
- Tridecyl amine ($C_{13}H_{27}NH_2$)
- 30 Tetradecyl amine ($C_{14}H_{29}NH_2$)
- Pentadecyl amine ($C_{15}H_{31}NH_2$)
- Nonadecyl amine ($C_{19}H_{39}NH_2$)
- 35 Eicosyl amine ($C_{20}H_{41}NH_2$)
- Heneicosyl amine ($C_{21}H_{43}NH_2$)
- 40 Docosyl amine ($C_{22}H_{45}NH_2$)
- Tricosyl amine ($C_{23}H_{47}NH_2$)
- 45 Tetracosyl amine ($C_{24}H_{49}NH_2$)
- Pentacosyl amine ($C_{25}H_{51}NH_2$)
- Hexacosyl amine ($C_{26}H_{53}NH_2$)
- 50 Heptacosyl amine ($C_{27}H_{55}NH_2$)
- Octacosyl amine ($C_{28}H_{57}NH_2$)
- 55 Nonacosyl amine ($C_{29}H_{59}NH_2$)

and the like.

Several of the above amines are known under other names, as for example, lauryl amine

($C_{12}H_{25}NH_2$)

myristyl amine ($C_{14}H_{29}NH_2$), mellisyl amine ($C_{30}H_{61}NH_2$), and cerotyl amine ($C_{26}H_{53}NH_2$).

It is within the province of the present invention to use the isomeric forms of the straight chain amines or any other amines which are sparingly soluble or substantially insoluble in water and which inhibit the foaming of the water or aqueous bath being treated. For example, the amine group may be attached to the first, or the second, or the third, or any other subsequent carbon atoms in the chain.

Examples of such isomeric forms are as follows:

Considering the normal straight chain primary amine, as set forth in the immediately preceding table, said amine being undecyl amine (formula $CH_3(CH_2)_{10}NH_2$), and the isomeric amine thereof is methyl, nonyl, methyl amine (formula $CH_3(CH_2)_8CHNH_2CH_3$).

Other isomers of this same normal amine are:

Ethylloctylmethylamine



Propylheptylmethylamine



Butylhexylmethylamine



Diamylmethylamine



Similar isomeric amines may be prepared from each of the amines listed in the immediately preceding table.

It may be stated that for nonacosyl amine ($C_{29}H_{59}NH_2$) there may be fifteen (15) corresponding isomers.

Secondary amines which are suitable for carrying out the present invention are:

Secondary heptylamine

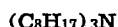


Secondary octyl amine



Tertiary amines suitable for carrying out the present invention are:

Tertiary octylamine



Tertiary octylamine



Secondary and tertiary amines typified by the above mentioned amines have a number of isomeric forms, which may be used in carrying out the present invention. Unbalanced straight chains or split chains result in many isomers for each amine having all alkyl groups the same.

Irrespective of to which carbon atom the amine group is attached, the material is a straight chain primary amine. Not only is it possible to use straight chain and split chain secondary and tertiary amines, but the isomeric forms of such amines may be used, and these compounds may differ from each other only in having an alkyl group substituted for one or both of the hydrogens in the amine group. If one hydrogen is substituted for, it would, of course, be a secondary amine, and if both of the hydrogens are substituted for, it would be a tertiary amine. Substituting alkyl groups for hydrogens in the amine group, would tend to result in products of lower water solubility, and, in some cases at least, it

would be possible to obtain secondary or tertiary amines which would have a lower water solubility than would the corresponding normal amine. However, the amine is substituted and irrespective of whether the amine is a straight chain amine or a split chain amine, the important point is that the amine, its substitution product or derivative, should be one which has negligible water solubility. While the amines of the character set forth are preferably aliphatic amines, it is within the province of the present invention to use aromatic amines which are sparingly soluble in water and which inhibit foaming in water having ingredients inducing foaming. The aliphatic amines may carry aromatic groups.

In carrying out the present invention, it is desirable to use aliphatic amines, their substitution products and derivatives, of high molecular weight which have a specific gravity less than water, so as to eliminate any tendency of these anti-foam agents to settle to the bottom of the treatment vessel. However, anti-foam agents of the character specified having a density greater than water may be used, provided it is used in combination with a material which will have a buoying effect upon it, as well as with other materials which will enable the anti-foam agent to be satisfactorily dispersed, and give the anti-foam and/or dispersing agent a body sufficient to render the dispersion permanent. It may be stated that aliphatic amines, their substitution products or derivatives, having a specific gravity greater than water and which are sparingly soluble, or substantially insoluble in the bath being treated, irrespective of whether the aliphatic amine, its substitution products or derivatives are aliphatic or aromatic compounds, may be prepared in various manners well known in the art by substituting in the amines themselves and by loading the side chains with materials such as halogen compounds or an aromatic nuclei. The amines used, their substitution products or derivatives, may comprise a mixture of saturated and unsaturated compounds.

Halogen substituted amines suitable for carrying out the present invention are prepared by chlorinating certain amines. This chlorination was effected by means of chlorine gas acting on a chloroform solution of the amine, or on the melted amine. Various amounts of chlorine may be added.

No specific formulae are assigned to the chlorinated amines set forth in the following table, due to the fact that these compounds may be chlorinated to various degrees and the resulting chlorinated compounds will vary accordingly.

The following table gives illustrations of chlorinated amines and shows the gain in weight in the amine during chlorination in terms of the final weight. In other words, taking the weight of the chlorinated amine as 100% each compound treated had its weight increased due to chlorination by the percentages set forth in the table.

Name of amine chlorinated	Increase in weight during chlorination in terms of final weight, per cent
Hexadecyl amine.....	13.0
Heptadecyl amine.....	13.2
Octadecyl amine.....	13.5

It may be stated that the degree of chlorination may vary considerably from the amounts set

forth in the table without greatly lessening the value of the anti-foam agent. It is desired to point out that during chlorination the amine increases in weight.

Although the amine may increase in weight due to chlorination, the density of the chlorinated material may be controlled so that it is less than water, or chlorination may be carried to a greater extent so as to produce a chlorinated product having a density greater than water, the densities in both cases being measured at the same temperature.

By introducing other groups into the herein set forth amines, a method is provided of increasing the specific gravity of the anti-foam agent. However, it is desired to point out that for most purposes, the specific gravity of the agent should not be increased so that it is greater than water, although as pointed out, such a material may be used, provided it is mixed with a buoying agent and a bodying agent, as set forth.

The high molecular weight amines and particularly the aliphatic compounds may be substituted with aromatic groups. However, the loading of the aliphatic amines with aromatic groups, as a usual thing, increases the density of the resulting compound so that it is greater than water, and as pointed out, it is desirable that the anti-foam agent have a specific gravity less than water.

It may be pointed out that the aromatic amines which have a density greater than water do not act very satisfactorily as boiler water anti-foam materials due to their high density. Further, many of these aromatic amines substantially insoluble in water have very high vapor pressures and have a greater tendency to steam distill which, of course, makes them, to a considerable extent, undesirable for the treatment of boiler water anti-foam materials, as the anti-foam agent, or a substantial portion thereof, will distill over. However, it may be stated that the mixed aliphatic and aromatic amines, and particularly those having a density less than that of water are satisfactory in carrying out the present invention. One way of preparing mixed aliphatic and aromatic amines is to load the aliphatic amines, and particularly the high molecular weight amines, with aromatic groups, preferably of high molecular weight, or vice versa, to load the aromatic amines with aliphatic groups, preferably of high molecular weight.

Very satisfactory results have been obtained when the present invention has been applied to waters containing sodium or potassium alkalinity, that is, water in which the sodium or potassium alkalis, or their equivalents, and particularly sodium or potassium hydroxides, carbonates or bicarbonates, exist in excess of that capable of combining with or existing in combination with calcium and/or magnesium ions present in the water.

Alkalinity of this type can exist naturally in the water or may be derived from zeolite treatment of the water, or may be derived in other ways.

The present invention may be applied to raw waters either hard or soft and beneficial results obtained. Water, which has been softened by the lime-soda-ash process or by phosphates, sodium silicates, or other alkaline treatment, may be treated with an anti-foam composition of the character herein set forth.

It is well known that many substances have decided anti-foam properties when used in con-

junction with normal types of water which are free from excess alkalinity, such as sodium alkalinity, or which have a low percentage of sodium alkalinity. Castor oil and sperm oil typify such substances.

When materials of this type are added to waters of excess alkalinity, and especially excess sodium and/or potassium alkalinity, poor or mediocre results are obtained in reducing the foaming tendency of the water. It seems probable that the foaming occurring in boiler water is the result of the concentration of soluble salts and insoluble solids in a state of suspension. In waters of excess alkalinity there may be present sodium and/or potassium bi-carbonates and/or carbonates, and there may be present sodium and/or potassium carbonates and/or hydroxides. Under conditions prevailing in an operating boiler, a large percentage of the bi-carbonates and carbonates originally present in the water are converted into hydroxides. It may well be that because of the presence of these hydroxides the usual anti-foam materials are ineffective when added to boiler waters having high or moderately high concentrations of alkali hydroxides or other alkali materials.

When oils of the above type are added to boiler water, there is a tendency for them to be saponified or react chemically with the alkali hydroxides or other alkali compounds, with the resultant formation of soluble sodium and/or potassium soaps. The foaming tendencies of sodium and potassium soaps are well recognized and the formation of such soaps accelerate the tendencies of the boiler water to foam.

The following is a specific example, illustrating such acceleration and foaming tendency. An experimental boiler operating at a pressure of 200 pounds per square inch, with an excess caustic alkalinity in the neighborhood of 200 grains per gallon, was treated with a standard anti-foam material containing 16% of castor oil by weight, the proportion being one-quarter pound of the castor oil material per 1000 gallons of water. Immediately after the introduction of the anti-foam material, a test showed no foaming occurring. One hour after the introduction of the anti-foam material, the amount of foaming occurring was approximately 25% greater than that taking place before the anti-foam material was added. The increase in foaming occurring one hour after the introduction of the anti-foam material, namely, castor oil, is due to the saponification of the same by the alkalines present in the boiler water.

Steam distillation of the usual anti-foam materials may, in some measure, reduce the effectiveness of these anti-foam materials in boiler water of high or excess sodium or equivalent alkalinity. However, since most of the usual anti-foam materials can be used effectively in water containing little or no sodium alkalinity, and their effectiveness maintained, to a large degree at least, for several hours, steam distillation of the anti-foam material is probably of minor importance.

In one form of the present invention, water containing alkalinity, and particularly sodium or potassium alkalinity, is treated with a material that is unsaponifiable and does not steam distill to any marked degree. Waters softened by base exchange processes, and especially those which have been treated with zeolites or waters having a high natural sodium carbonate or sodium bicarbonate alkalinity are typical of waters hav-

ing foaming properties and which may be treated in accordance with the present invention, which resides not only in said method, but also in the utilization of a particular class of anti-foam materials, and the method of preparing the same. While the average operating boiler pressure is around 200 pounds per square inch, it is to be understood that the present invention is applicable to boiler pressures materially higher or lower than 200 pounds per square inch.

The amines of the present invention may be mixed with a dispersing agent and in the narrower form of the invention, the preferred dispersing agent is tannin, as will be hereinafter more fully pointed out. The dispersing properties of the amine may be substantially increased by passing the amine through a colloid mill or any other equivalent device, in order that shearing may occur and thereby reduce the particle size of the amine. Passage of the amine, together with or without a dispersing agent and/or a bodying agent, functions to cause the composition to become more active as an anti-foam agent. Therefore, it is one of the objects of the present invention to increase the activity of the amine and the composition containing the same by shearing the composition and its ingredients by passing through a colloid mill.

Another object of the present invention is to, in a measure, control the stiffness of the compound by controlling the particle size of the anti-foam agent and its ingredients, as will be more fully hereinafter pointed out.

It may be stated that three principal typical classes of dispersing agents are available. The first class comprises inorganic colloidal material, such as clays or bentonite; the second class, organic materials which contain appreciable quantities of soap in one form or another; and the third class, organic materials which are characterized by colloidal properties and which contain no soap of any kind. This third class of materials includes the extracts of various woods and barks which would normally be referred to as tannin extracts; extracts of various aquatic plants, such as seaweeds or kelp; and extracts of certain plants and shrubs, such as cactus plants.

Clays or bentonite may, of course, be used, but the disadvantages of this type of material makes it inadvisable to use it as the sole dispersion agent, since it does not lend itself to the very great dispersion that is necessary when a very small quantity of an anti-foaming compound is dissolved in a relatively large amount of boiler feed water. However, the clays or bentonite may be used as the dispersion agent when mixed with other materials, as hereinafter set forth.

The soap dispersion agents may under some circumstances be used, but certainly not where there is an excess of alkali present, because the soap, in this case, remaining water soluble would tend to counteract the anti-foam properties of the anti-foam agent, and, moreover, in some cases, function to increase the foaming properties of the boiler water instead of decreasing them.

Investigation has shown that tannin is a very desirable dispersing agent, because at least when waters having alkaline constituents are treated, and particularly boiler waters, the tannin has better dispersing properties than the clays or soap, while at the same time it does not have the disadvantages of the latter classes of materials.

It may be pointed out that tannin in certain

cases and in certain types of waters, has fairly good anti-foam properties and, therefore, the use of tannin in conjunction with a more active and anti-foam agent results in a composition having anti-foam properties superior to that of either the materials used separately. Further, the tannin acts as an active dispersing agent for the more active or primary anti-foam material, and this is highly desirable in a good anti-foam composition. Again, the tannin performs the function of conferring upon the resulting composition non-corrosive properties. This is due to the tendency of the tannin extract and similar materials to absorb dissolved oxygen from the boiler feed water or from any other water containing oxygen, which oxygen, if not removed, is one of the principal causes of boiler corrosion. Tannin, of course, is an example of a material which is an active dispersing medium and also acts as a corrosion inhibitor to prevent corrosion of the boiler metal. It is within the province of the present invention in its broad form to use other equivalent materials which perform the same functions as the tannin performs.

The composition may have present a viscosity-increasing agent or bodying material. A number of compounds may be used as the bodying agent, but it is preferable to use corn meal or a material containing starch. The corn-meal or starch acts not only as a bodying material, but also as an additional dispersing agent and increases the dispersion characteristics of the composition. In accordance with one form of the present invention, the anti-foam composition has present a primary dispersion agent, and a secondary dispersion agent, the secondary dispersion agent preferably acting also as a bodying agent or to increase the viscosity of the anti-foam composition, which, of course, contains anti-foam agents, as hereinbefore pointed out.

The increase in the viscosity of the anti-foam composition is desirable since this prevents separation of the active anti-foam constituents from the remainder of the composition.

The following are examples of methods which may be used to obtain the bodying effect.

In one method the meal or starch is heated in the presence of added water or that contained in the liquid tannin extract to a temperature high enough to produce a hydrolysis of the meal. This hydrolyzed meal upon cooling takes on the form of starch paste and acts to increase the viscosity of the anti-foam composition in proportion to the amount of starch or meal used. The amount of bodying agent used in the anti-foam composition may, of course, vary.

In carrying out the present invention, the primary, secondary or tertiary anti-foam agent may be a simple amine saturated or unsaturated, or a mixed amine, saturated or unsaturated. Further, the primary anti-foam agent may be a mixture of simple amines saturated or unsaturated, or a mixture of mixed amines, saturated or unsaturated. The amine compound or the free amine may be formed in situ by decomposition of a suitable salt, said salt upon being added to the water, converting at least a part of the free salt to the free amine.

The compounds which are useful in carrying out the present invention are generally represented by the following formula:



In said formula R denotes an alkyl group and/or

an aryl group and/or an aralkyl group, said aryl group and/or aralkyl group preferably not substantially decreasing the insolubility of the anti-foam material in the water or bath being treated.

R' and R'' each represent hydrogen and/or an alkyl group, and/or an aryl group, and/or an aralkyl group. The alkyl, aryl and aralkyl groups may have introduced therein one or more substituents. In other words, by the terms "alkyl" "aryl" or "aralkyl" group is intended to include groups containing substituents, as for example, chlorine groups, hydroxy groups and oxyalkyl groups; these terms, of course, are to be interpreted as also including unsubstituted groups. Within the scope of the term "alkyl group" is also included cycloalkyl, as well as straight and branched chain alkyl groups.

The above formula is intended to cover the primary, secondary and tertiary amines, and their derivatives or substitution products. When one hydrogen is replaced in NH_2 the resulting compound may be designated RNH_2 which contains the amino group NH_2 . When two hydrogens are replaced, the secondary amine as represented by the formula $\text{RR}'\text{NH}$ contains an imino group, and when three hydrogens are replaced the tertiary amine is formed, having the formula $\text{RR}'\text{R}''\text{N}$.

In the preferred form of the invention, the amines which it is desired to use for the treatment of boiler water are those amines which do not steam distill to any substantial extent. This is one of the reasons why it is desired to use amines or their substitution products or derivatives, coming within the above general formula, which have high molecular weights. An additional reason for the use of such compounds is that those with high molecular weights are substantially insoluble in the water being treated, and further show little tendency to saponify with the ingredients of the bath. It may be stated that branching of the chain lowers the boiling points of even the high molecular weight amine compounds coming within the above formula, but if the boiling point is not greatly reduced, these branch chain compounds may be used in the treatment of boiler water. It is for the above reasons that in the preferred form of the invention, the compounds coming within the scope of the above general formula should have at least eleven (11) carbon atoms present in the amine molecule.

The following is an illustrative example of how the present invention may be carried out, there being utilized, in addition to the amine anti-foam agent, a dispersing agent and/or a bodying agent. While it may not be necessary in some substances to use a dispersing and/or bodying agent, as a general rule, it is desirable.

The above indicates what is meant by the term "amine having a high molecular weight." By this term it is intended to cover amines of the character set forth having eleven (11) or more carbon atoms. The higher amines of the series $\text{C}_n\text{H}_{2n+1}\text{N}$ which have given very satisfactory results are heptadecyl amine and stearyl amine. Polysubstituted amines and particularly those having eleven (11) or more carbon atoms present in the amine molecule may also be used. The amine, such as heptadecyl amine or stearyl amine may be mixed with a small percentage of corn meal and a predominating quantity of a liquid tannin extract well known in the prior art, and the mixture is heated to a temperature sufficient to produce a hydrolysis of the meal and to gelatinize

the final product. Satisfactory results have been obtained by heating the mixture to about 180° F. Higher temperatures may be used. This mixture is fed into the boiler in the form of a water suspension.

As indicated, the preferred form of the anti-foam composition for introduction into the boiler feed water is that of a gelatinized product. Such a gelatinized composition may be made by mixing together an amine, such as heptadecyl amine, stearyl amine, or any other amine or amine mixture herein set forth with corn meal and tannin extract.

The ingredients may be mixed in suitable proportions, of which the following Tables I to V are illustrative:

Table I

(1) Corn meal—2%, tannin extract—94%, amine—4%
(2) Corn meal—4%, tannin extract—88%, amine—8%
(3) Corn meal—6%, tannin extract—78%, amine—16%
(4) Corn meal—8%, tannin extract—67%, amine—25%
(5) Corn meal—8%, tannin extract—57%, amine—35%

In general, the amine content of the mixture may vary between about 1% to 2% to 35%.

The above percentages are merely illustrative as the amount of tannin extract and aliphatic amine, its derivatives or substitution products, and may vary within the limit of the maximum and minimum above set forth and still come within the spirit of the present invention. As hereinbefore pointed out, the primary anti-foam base, such as the aliphatic amine, its substitution product or derivative, may be used by itself, but it is desirable that the primary anti-foam agent be used in conjunction with the tannin, as the tannin assists in the dispersion, and further is in itself an anti-foam agent. It is preferred to form a gelatinized product of the ingredients, but here again, it is within the spirit of the present invention to use the primary anti-foam agent in an anti-foam composition which is not reduced to paste form.

Instead of using corn meal or starch as the viscosity-increasing or bodying agent, various other such agents may be used, as for example, dextrine. When using dextrine, satisfactory results have been obtained when the mixture contained from 5% to 50% of dextrine, which is a degradation product of starch. Instead of using corn meal, starch or dextrine, other bodying agents may be used. Gums, such as gum tragacanth, gum acacia and locus bean gum, which are additional examples of suitable bodying agents, give good results.

It has been ascertained that excellent results are obtained when the bodying material is one which will produce borate ions, as for example, borax may be used as the bodying agent, or the borax may be mixed with an additional bodying agent, such as corn meal or dextrine.

The following examples illustrate how the dispersion agents and the bodying agents may be varied:

Table II

Amine	Tannin extract	Corn meal
Per cent	Per cent	Per cent
2	92	6
5	89	6
10	84	6
15	79	6
20	75	5
30	66	4
35	61	4

Table III

Amine	Tannin extract	Bentonite	Corn starch
Per cent	Per cent	Per cent	Per cent
2	87	5.0	6.0
5	84	5.0	6.0
10	79	5.0	6.0
15	74	5.0	6.0
20	70	5.0	6.0
30	61	5.0	6.0
35	56	5.0	6.0
2	82	10	6.0
5	79	10	6.0
10	74	10	6.0
15	70	10	5.0
20	65	10	5.0
30	56	10	4.0
35	51	10	4.0

Table IV

Chlorinated amine	Tannin extract	Dextrine	Borax
2	85	12	1.0
5	82	12	1.0
10	77	12	1.0
15	72	12	1.0
20	67	12	1.0
30	57	12	1.0
35	52	12	1.0

In the above illustrative example, borax used as the bodying agent, may be replaced by boric acid or by and water soluble borate, or by any substance capable of giving borate ions when dissolved in water. The amount of borax may vary over wide limits, the minimum being approximately one-eighth ($\frac{1}{8}$) of one per cent (1%), and the maximum around five per cent (5%).

Table V

Hydroxy amine	Tannin extract	British gum
2	86	12
5	83	12
10	78	12
15	73	12
20	68	12
30	58	12
35	53	12

It is desired to point out that the above examples are merely illustrative of suitable combinations of dispersing agents and bodying agents, together with amines, chlorinated amines or hydroxy amines prepared as hereinafter set forth, and that various other dispersing agents and bodying agents may be used and still come within the spirit of the present invention.

The alkali phosphates, such as meta-sodium phosphate, mono-sodium phosphate, di-sodium phosphate and tri-sodium phosphate may be used as the dispersing agents.

Satisfactory results have also been obtained by using as the dispersing agent a sodium salt of the sulphuric acid esters of high molecular weight alcohols, such compounds being commercially known under the trade name of "Orvus," "Gardinol" or "Dreft." These compounds included under the aforesaid designations, are known as sodium lauryl sulphate. In general, it may be stated that these materials may be designated as the sodium sulphates of high molecular weight alcohols having 10 to 14 carbon atoms.

It is clear from the above that the bodying agent may be an inorganic or an organic com-

pound. Further, it is desired to point out that many of the bodying agents set forth also act as dispersing agents, and in the preferred embodiment of the present invention, the bodying agents also act as dispersing agents. It is not desired to limit the present invention to any particular inorganic or organic bodying agent. Broadly, any bodying agent may be added which will function to increase the viscosity of the mixture, and preferably also assist in effecting a satisfactory emulsion or dispersion.

In some cases, the bodying agent may be a mixture of organic bodying agents, or may be a mixture of inorganic bodying agents, or the bodying agent may be a mixture of organic and inorganic compounds. In either case, it is preferred that the bodying agent be a dispersing agent.

While usually the amount of bodying agent will vary from 2% to 8%, it may be much higher, as for example, when using dextrine, up to about 50% by weight of the mixture may be dextrine, and again it is not necessary that in some of the bodying agents that the lower limit be 2%. Less than 2% may be used, and while 2% may be considered a satisfactory lower limit for starch, if the starch is used in conjunction with other thickening agents, such as a gum, then the starch may be reduced to less than 2%.

The primary anti-foam agent, such as the aliphatic amine, its derivatives or substitution products, may be mixed with a dispersing agent, preferably one which is also an anti-foam agent, as for example, tannin, and with a bodying agent, such as corn meal and starch, and these materials, without heating, may then be passed through a colloid mill. In a mill of this character, a shearing occurs which results in reducing the particle size of the starch and thereby greatly increases the bodying effect of the bodying agent over what it is in the cold composition before the latter has been put through the colloid mill. While the passage of the material through the colloid mill favorably reduces the particle size of the starch, it also effectively operates upon the remaining ingredients of the composition, and thereby forms a permanent emulsion. It is thought to be broadly new to form a permanent emulsion containing an anti-foaming agent of the character described, and also broadly new to form a permanent emulsion of an anti-foaming agent of the character described, the dispersing agent and a bodying agent. The reduction in the size of the primary anti-foam agent, as for example, the aliphatic amine, produces a much more active anti-foam agent.

Heretofore, there has been set forth the heating of the anti-foam composition to a temperature sufficient to produce a hydrolysis of the bodying agent, such as corn meal, starch and the like. The heated combination after the hydrolysis of the starch may be passed through a colloid mill or its equivalent to produce a very effective anti-foam composition. It may be pointed out that if the anti-foaming composition herein described is heated sufficiently to result in hydrolysis of the starch, dextrine or like product before passing the same through the colloid mill, that there will still be produced a satisfactory dispersion of the primary anti-foam agent despite the fact that the material containing the hydrolyzed starch will become very much stiffer in composition if it has been allowed to cool and set. When the unheated anti-foam composition is passed

through the colloid mill, a satisfactory dispersion may be obtained in like manner but the final composition will be somewhat thinner, due to the lack of a gel being present, the latter resulting from the hydrolysis of the cooked starch or like agent.

It may be pointed out that by passing the composition through the colloid mill, the particle size of the suspended material is reduced to a greater extent than that which is obtained by the use of any of the ordinary dispersing agents or dispersing equipment. It may be stated that it is this great reduction in the particle size of the suspended material which is responsible for the stiffening effect when the anti-foam emulsion is passed through the mill. It may also be pointed out that while the use of the colloid mill does result in the stiffening of the herein described anti-foam composition, this stiffening effect is a minor one, as compared to the stiffening effect which is accomplished by the use of a bodying agent.

The times when it is desirable to use a stiffer or thinner anti-foam composition are not dependent upon the type of water which is to be treated, but rather on the method of introducing the anti-foam composition and the climatic conditions to which the anti-foam composition is subjected during storage. For example, when it is the practice to use hot water in digesting the anti-foam composition before its introduction into the boiler, it is usually desirable to use a stiffer type of anti-foam composition than is used if the cold water is a digesting medium. Stiffer emulsions as a rule are more stable than the thinner ones, and if hot water is used as the digesting medium a somewhat stiffer and, therefore, a somewhat more stable anti-foam emulsion can be satisfactorily digested. When using cold water, it is sometimes difficult to satisfactorily break up or digest a stiff emulsion, and for this reason it is necessary that the product used be somewhat thinner. It is also commonly appreciated that with higher temperatures, the emulsions tend to become somewhat thinner. When anti-foam material is stored in very hot warehouses or other places where temperatures in the neighborhood of 90° or 100° F. are present, thinner emulsions become quite fluid, and the tendency for the conglomeration of the suspended particles is increased due to the lower viscosity of the product. Where an anti-foam composition is liable to be subjected to conditions typified by those above mentioned, it is desirable to use a stiffer or heavier product. On the other hand, during midwinter, when the anti-foam composition may be subjected to a relatively low temperature, it is desirable to use a thinner product.

In view of the above, in accordance with the present invention, the stiffness of the anti-foam composition may be controlled by the use of a bodying agent alone, or by the use of a bodying agent and the passage of the material through a colloid mill to reduce the particle size of the suspended material. To decrease the stiffness, less bodying agent is used, and to increase the stiffness, more bodying agent is used. The stiffness may be controlled even though the bodying agent is not hydrolyzed.

Anti-foam compositions of the character set forth may be stabilized, or at least their stabilization may be promoted, by the proper adjustment of the pH value of the composition.

In most cases, although not in every case, the emulsion or dispersion is more stable if the pH

of the composition is maintained at the neutral point or just slightly alkaline. In other words, it is best to maintain the pH of the composition between 7 and 8, and this is especially true when using starch, corn meal, dextrine or the gums.

A paste mixture prepared by any of the methods set forth and containing a primary anti-foam agent, a secondary anti-foaming agent, which preferably has dispersing properties, and a bodying agent of the character herein set forth may be added to boiler water to prevent foaming thereof. More specifically, any of the compositions herein set forth may be added to the boiler water in the ratio of one-quarter pound of the composition per 1000 gallons of water. The amount which may be added is strictly illustrative, and is not to be taken by way of limitation. Obviously, the amount of anti-foam material which is added to the water will depend upon the characteristics of the water. For example, in another experiment it was found that as low as one-twentieth ($\frac{1}{20}$) of a pound of the anti-foam composition per 1000 gallons of water was satisfactory. In still another case, two (2) pounds of the anti-foam composition per 1000 gallons of water positively inhibited the anti-foam tendency of the boiler feed.

The above mixtures and similar mixtures were added to water of the character that the castor oil, previously referred to, was added, and the conditions of the tests were the same.

Tests taken immediately after the introduction of the anti-foam composition showed no foaming occurring. Tests made two and one-half ($2\frac{1}{2}$) hours after the introduction of the anti-foam material showed the foaming to be practically nil. Tests which were made after continuous heating of the anti-foam material in the boiler water, under the above conditions, for eight (8) hours, showed a tendency to foam, which was only a small fraction of the foaming occurring before the anti-foam was added. After twenty (20) hours, the tendency to foam was not quite as great as that exhibited by the untreated water. Even in the presence of the anti-foam material, there is some tendency to foam, and the amount of foaming in the presence of the anti-foam material may vary from a very small percentage to 25% to 40% of the foaming that occurs before the anti-foam material is added.

The compounds herein set forth give markedly superior results when treating water containing excess alkalinity. If castor oil, which is a well known anti-foaming agent for water which does not contain excess alkalinity, were used, the oil would become saponified and thereby rendered ineffective and/or harmful. In raw water and water softened in any well known manner, as for example by the lime-soda-ash process, the amines as hereinbefore described are also effective.

It has been previously pointed out that admirable results have been obtained with a bodying material which will produce borate ions. The material producing the borate ions may be used alone as the bodying agent, or it may be mixed with additional bodying agents. It has been previously pointed out that dextrine may function as the bodying agent. However, the composition may be so proportioned that the bodying effect is obtained by the material which will produce the borate ions and when this is true, any of the prior art dispersing agents may be used, but

preferably those hereinbefore mentioned and more particularly a carbohydrate dispersing medium, such as corn meal, dextrine, or starch degradation products. Where in the specification it is stated that corn meal or starch may be used as the bodying agent, it is, of course, understood that the degradation products of corn meal or starch may be used as the bodying agent.

There is provided, therefore, in accordance with one form of the present invention, a composition for treating an aqueous bath and particularly waters of the character hereinbefore set forth, said composition containing an organic anti-foam agent substantially insoluble in the bath, a dispersing agent therefor and a bodying agent including a constituent provided with borate ions. Preferably, the dispersing agent includes tannin and dextrine, and a carbohydrate material, such as starch, dextrine, or starch degradation products.

It is broadly novel to use as a bodying agent a constituent provided with borate ions, and the applicant's invention in one of its forms is directed to this novel feature, irrespective of the anti-foam agent, or even the dispersing agents, it being recognized that in some few cases the dispersing agent, with the exception of the tannin extract, may be eliminated.

While the tannin extract herein set forth is preferably prepared from chestnut oak, it is obvious that tannin extracts may be used in accordance with the present invention which have been prepared from other well known prior art tannin-containing materials.

The present application is a continuation-in-part of abandoned application Ser. No. 579, filed January 5, 1935.

The expression "comprising introducing into the bath a composition containing as its essential anti-foam agent a mixture of saturated and unsaturated aliphatic amines," or equivalent expressions as used in some of the claims, is intended to cover the introduction of the mixture of amines into the bath or the bath into the mixture of amines.

I claim:

1. The method of conditioning an aqueous bath having ingredients present inducing foaming therein comprising introducing into the bath a composition containing as its essential anti-foam agent a mixture of saturated and unsaturated aliphatic amines of high molecular weight and each containing at least eleven carbon atoms in an alkyl radical thereof, said amines being characterized by the properties of being insoluble in the bath and showing little tendency to saponify with the ingredients of the bath, the anti-foam agent being present in an amount sufficient to inhibit foaming of the bath.

2. The method of conditioning an aqueous bath having excess alkalinity inducing foaming therein comprising introducing into the bath a composition containing as its essential anti-foam agent a mixture of a saturated and an unsaturated aliphatic amine each of high molecular weight and each containing at least eleven carbon atoms in an alkyl radical thereof, said amines being characterized by the properties of being insoluble in the bath and showing little tendency to saponify with the ingredients of the bath, the anti-foam agent being present in an amount sufficient to inhibit foaming of the bath.

3. The method of conditioning boiler water having ingredients present inducing foaming therein comprising introducing into the boiler

water a composition containing as its essential anti-foam agent a mixture of a saturated and an unsaturated aliphatic amine each of high molecular weight and each containing at least eleven carbon atoms in an alkyl radical thereof, said amines being characterized by the properties of being insoluble in the boiler water and showing little tendency to saponify with the ingredients of the boiler water, the anti-foam agent being present in an amount sufficient to inhibit foaming of the boiler water.

4. The method of conditioning boiler water having excess alkalinity inducing foaming therein comprising introducing into the boiler water a composition containing as its essential anti-foam agent a mixture of a saturated and an unsaturated aliphatic amine each of high molecular weight and each containing at least eleven carbon atoms in an alkyl radical thereof, said amines being characterized by the properties of being insoluble in the boiler water and showing little tendency to saponify with the ingredients of the boiler water, the anti-foam agent being present in an amount sufficient to inhibit foaming of the boiler water.

5. The method of claim 1 wherein the composition with which the bath is treated has tannin present.

6. The method of conditioning an aqueous bath having ingredients present inducing foaming therein comprising introducing into the bath an anti-foam composition containing a tertiary aliphatic amine having at least eleven carbon atoms in an alkyl radical thereof, said compound being characterized by the properties of being insoluble in the bath and showing little tendency to saponify with the ingredients of the bath, the anti-foam agent being present in an amount sufficient to inhibit foaming of the bath.

7. The method of conditioning an aqueous bath having ingredients present inducing foaming therein comprising introducing into the bath an anti-foam composition containing a secondary aliphatic amine having at least eleven carbon atoms in an alkyl radical thereof said compound being characterized by the properties of being insoluble in the bath and showing little tendency to saponify with the ingredients of the bath, the anti-foam agent being present in an amount sufficient to inhibit foaming of the bath.

8. The method comprising conditioning boiler feed water having alkaline ingredients present inducing foaming therein by introducing into said boiler feed water an anti-foam composition containing a tertiary aliphatic amine having at least eleven carbon atoms in an alkyl radical thereof, and being characterized by the properties of being insoluble in the boiler feed water and showing little tendency to saponify with the ingredients of the boiler feed water, said tertiary amine being present in an amount sufficient to inhibit foaming of the boiler feed water.

9. The method comprising conditioning boiler feed water having alkaline ingredients present inducing foaming therein by introducing into said boiler feed water an anti-foam composition containing a secondary aliphatic amine having at least eleven carbon atoms in an alkyl radical thereof, and being characterized by the properties of being insoluble in the boiler feed water and showing little tendency to saponify with the ingredients of the boiler feed water, said secondary amine being present in an amount suf-

ficient to inhibit foaming of the boiler feed water.

10. The method of claim 8 in which tannin is present in the anti-foam composition.

11. The method of claim 9 in which tannin is present in the anti-foam composition.

12. The method comprising conditioning boiler feed water having alkaline ingredients present inducing foaming therein by introducing into said boiler feed water an anti-foam composition containing tannin, a viscosity-increasing material and a tertiary aliphatic amine having at least eleven carbon atoms in an alkyl radical thereof, and being characterized by the properties of being insoluble in the boiler feed water and showing little tendency to saponify with the ingredients of the boiler feed water, said ter-

tiary amine being present in an amount sufficient to inhibit foaming of the boiler feed water.

13. The method comprising conditioning boiler feed water having alkaline constituents present inducing foaming therein by introducing into said boiler feed water an anti-foam composition containing tannin, a viscosity-increasing material, and a secondary aliphatic amine having at least eleven carbon atoms in an alkyl radical thereof and being characterized by the properties of being insoluble in the boiler feed water and showing little tendency to saponify with the ingredients of the boiler feed water, said secondary amine being present in an amount sufficient to inhibit foaming of the boiler feed water.

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