United States Patent Office 3,056,687 Patented Oct. 2, 1962

3,056,687

ANTI-FOAMING AGENTS FOR AQUEOUS ALKALINE PROTEINACEOUS ADHESIVE SOLUTIONS AND THE LIKE

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No Drawing. Filed June 30, 1959, Ser. No. 823,836
21 Claims. (Cl. 106—154)

This invention relates to improvements in anti-foaming compositions for foam abatement in aqueous alkaline proteinaceous adhesive solutions and the like, and more particularly relates to improvements in foam inhibitors and improvements in the art of defoaming such adhesive solutions as used commercially in wood product lamination arts, and the like.

It is well known that alkaline aqueous protein solutions and the like show a marked tendency to foam and there are many examples of the use of such solutions where control of foaming is essential to the success of the operation.

In the manufacture of plywood using a protein adhesive such as an aqueous alkaline colloidal solution of soybean flour as described in U.S. Patent No. 1,691,661, the application of the adhesive by a double roll coating machine to the wood veneers prior to laying up the veneers in a plywood assembly necessitates control over the foaming tendency of the soybean adhesive. If foam develops in such a solution a pronounced change in specific gravity of the solution takes place and as a direct consequence less and less weight of adhesive is spread since roller applicators spread adhesive on a constant volume basis.

Effectiveness and suitability of a given composition as an anti-foaming agent for a given specified foamable liquid or dispersion, such as aqueous alkaline proteinaceous adhesive solutions, are authoritatively recognized as very difficult problems to resolve, except by empical discovery. A given composition of known efficacy and suitability in one field will have a markedly different functional characteristic in a seemingly analogous field of utility.

One recognized authority concerning anti-foaming agents ("Foams: Theory and Industrial Applications," by J. J. Bikerman et al., chapter 15 entitled "Chemical Anti-foaming Agents," pp. 297–321, published in 1953 by Reinhold Publishing Co., New York, N.Y.) reports textually an excellent and comprehensive treatment of various defoamers in various fields, with an extensive bibliography of patent and literature art. As to the question of whether trends can be determined with respect to the effectiveness of defoamers, this text (at page 297) presents a good analysis of the problem and indicates:

". . . it was hoped that chemical types might show a certain specificity in their action toward foams. . . . Because of several complicating factors this rather ambitious hope was not realized. First, the action of a foam inhibitor cannot be predicated by analogy, and generalizations can be misleading. . . ."

Recognizing the empirical nature of the art, it is an object and feature of the present invention to provide improved anti-foaming agents for adhesive solutions of the character indicated, wherein the anti-foaming agent contains a known anti-foaming agent for alkaline, proteinaceous adhesive solutions, such as a liquid alcohol, a tri-alkyl phosphate, a tri-alkyl phosphonate, a tri-alkoxy phosphate, a substituted amine surface active agent, and the like, and includes in composition therewith a saturated fatty acid materially and unexpectedly improving the effectiveness and efficiency of the resulting composition as an anti-foaming agent in said solutions, it being also known that a saturated fatty acid of itself has a deleterious effect on the foaming action of this type of foamable solution. The term "solutions" in this regard in the specification and following claims is used to define and include such adhesive solutions, dispersions and colloidal suspensions.

It is a further object and feature of the present invention to provide improved anti-foaming agents for solutions of the character indicated, wherein an effective proportion of one or more of the ingredients of such anti-foaming agent can be readily incorporated in a proteinaceous material, such as soybean meal or flour, to provide a premixed, essentially dry composition readily placed in aqueous solution at the situs of use as an alkaline protein-base adhesive solution, the resulting defoamed solution exhibiting marked resistance to foaming during application and use in the fabrication of laminated products according to standardized commercial procedures.

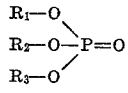
With these and such other objects and features in view, as will be apparent from the following description, the present invention contemplates improved anti-foaming agents for solutions of the character indicated, wherein such agents include, in composition with a high molecular weight saturated fatty acid, one or more of the following known defoamant ingredients in the field; an alcohol, a tri-alkyl phosphate, a tri-alkyl phosphonate, a tri-alkoxy phosphate; a substituted amine surface active agent, and mixtures thereof, together with a suitable spreader oil as an extender or spreading agent, as desired.

Within the scope of the present invention, as will be evident from the following typical examples thereof, by the term high molecular weight saturated fatty acid is meant a saturated aliphatic mono-carboxylic acid having a molecular weight of at least 228. Such fatty acids as may be advantageously employed in carrying out my invention are myristic, palmitic, stearic, arachitic, behenic acids and the higher homologues thereof, and mixtures thereof. It will be understood that technical grades of these fatty acids usually contain various minor amounts of fatty acids of molecular weight lower than myristic as well as varying incidental amounts of unsaturated fatty acids. These technical grades of the indicated saturated fatty acids are demonstrably satisfactory for purposes of the anti-foaming compositions of the present invention and are to be construed as included within the terms indicated. However, as demonstrated specifically in certain examples set forth below, non-saturated fatty acids such as oleic and linoleic are not suitable for purposes of the present invention, presumably because of the unsaturated character of the molecular structure.

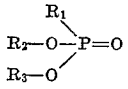
In the context of the present invention, by the term alcohol of a monohydric type is meant a primary, secondary, or tertiary alcohol having at least 4 carbon atoms, which alcohol is aliphatic, cyclic or otherwise non-aromatic in nature and is liquid at normal room temperature. A type of alcohol typifying the present invention and commonly used for foam abatement purpose is steam distilled pine oil (commercial alpha-terpineol). The term alcohol as employed herein also is to be construed as including technical grades of such alcohols. In connection with the nature of the alcohol ingredient of the anti-foaming compositions as contemplated by the present invention, it is theorized that an important property of the alcohol in this connection is the low water solubility thereof and the applicable alcohols may be readily demonstrated and distinguished by a comparison of the relative water solubility of butyl alcohol and propyl alcohol in this regard. Thus, the least soluble of the butyl alcohols is butanol-1, having a solubility of 9 parts per 100 in water at 15° C., which degree of solubility has been demonstrated in the following examples as having advantageous anti-foaming characteristics when employed in composition with stearic acid as herein contemplated, whereas the propyl alcohols are infinitely miscible with water and do not exhibit the requisite anti-foaming properties when employed as the alcohol ingredient in com-

positions according to the present invention. Thus, the alcohol contemplated by the present invention may be otherwise expressed as an aliphatic, cyclic or otherwise non-aromatic liquid carbinol of a monohydric type, having at least 4 carbon atoms and having a water solubility of 9 parts or less by weight per 100 parts of water at 15° C.

Within the scope of the present invention, by the terms tri-alkyl phosphate, tri-alkyl phosphonate, and tri-alkoxy phosphate are meant compounds conforming to one of the following formulas:

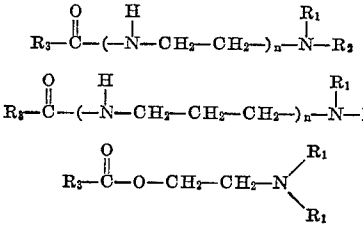


a phosphate ester where R_1, R_2, R_3 are alkyl or alkoxy groups.



an alkyl phosphonate where R_1 is an alkyl group, R_2 and R_3 are alkyl or aralkyl groups.

Substituted amine surface active agents which are especially suitable for use in my anti-foaming compositions are those which conform to one of the following formulas:



where R_1 and R_2 are an H, or an alkyl, aralkyl, or hydroxy substituted alkyl group, R_3 is an alkyl, alkenyl, naphthenyl, or aralkyl group having at least 4 carbon atoms, and n is 1, 2, 3, or 4.

Typical surface active products of this nature are the reaction products of palmitic acid and ethylene diamine, stearic acid and propylene diamine, oleic acid and diethylene triamine, naphthenic acid and tri-ethylene tetramine, pelargonic acid and tetra-ethylene pentamine, phenyl-propionic acid and di-ethylene triamine, stearic acid and di-methyl ethanolamine, and combinations of any of the above acids with any of the above amines.

It is to be noted that in the foregoing compounds the organic acid is combined as an ester or amide and that at least one nitrogen atom is available for salt formation with the fatty acid in the formulation of the surface active agent.

By the term extender or spreading agent is meant a non-volatile hydrocarbon diluent which is substantially insoluble in water and which does not attack production equipment rolls, etc., during production use of the solution, which diluent has a kauri-butanol value (ASTM Designation D–1133–50T) of about 40 or less. Common examples of such extenders include petroleum distillates such as kerosene, fuel oil, diesel oil and light petrolatum, for example.

In connection with the various examples typifying the present invention enumerated below, it is to be noted that such examples demonstrate that while liquid alcohols, or phosphates, or phosphonates have characteristic anti-foaming properties in a protein-base adhesive solution and the like, such properties are materially improved by combining therewith an appropriate amount of saturated fatty acid. Further, other examples below indicate that, while according to the present invention and discovery fatty acids have unexpected and remarkable properties in combination with the indicated alcohols, phosphates or phosphonates, saturated fatty acids of the character here presented do not of themselves exhibit substantial anti-foaming properties in such protein adhesive solutions but on the contrary actually, in many cases, increase the tendency of the solution to foam.

In the following examples, where a substituted amine surface active agent is employed, the organic acid and the amine indicated in each instance were reacted in the following manner. 100 parts of the organic acid were mixed with 15 parts of the amine in a stainless steel kettle equipped with an agitator and a Dowtherm heating system. Each such mixture exhibited exothermic reaction and further heating was begun immediately. After 30 minutes of heating the temperature of the reaction mass was maintained at 145° C., the reaction mass at such temperature exhibiting a steady effervescence. After 30 minutes' reaction at about 145° C. the bubbling practically subsided. The reaction temperature of the mass was held between about 145° C. and about 155° C. for a total of about 4 hours. At the end of the reacton period the reaction mass was cooled and while still molten was poured into trays.

In the following examples, except where otherwise indicated, the alkaline, proteinaceous adhesive test solution was prepared and the effect of the various anti-foaming compounds or compositions thereon was determined in the following manner. 400 parts of soybean flour (such as "Soytex," obtained from the Spencer-Kellogg Company of Decatur, Illinois) was mixed with 1000 parts water at 70° F., and 16 parts of the indicated defoamer compositions were mixed therewith in a mechanical mixer for three minutes. At the end of this period the resulting mixture was free from lumps. 40 parts of calcium hydroxide (such as "Shell" Brand, obtained from the Shell Chemical Company), suspended in 230 parts of water was added to the previous mix and mixed thoroughly with continuous mechanical agitation for three minutes. 44 parts of a 50% sodium hydroxide (NaOH) solution were added and thoroughly mixed for one minute. 100 parts of sodium silicate (such as "N" Brand, obtained from the Philadelphia Quartz Company) were added and mixed one minute. 6 parts of a liquid mixture containing 75% carbon bisulfide and 25% carbon tetrachloride by weight were added and mixed two minutes. The resulting alkaline proteinaceous adhesive solution was then removed from the mixer and stored, and is essentially in the form used in the manufacture of plywood.

During the experiments to test the relative efficiency of various anti-foaming compositions for foam abatement, a laboratory foam machine closely simulating actual production conditions was utilized. The foam machine employed consisted of a steel roll 8.5 inches in diameter and 6.5 inches long rotated at 144 r.p.m. in an attached wedge shaped hopper. The total capacity of the hopper was 1200 cc. and approximately 880 cc. of glue solution was charged in the hopper in each instance of experimental test. The gap or slit where the hopper and the roll almost come in contact was .030 inch wide. The action of the rotating roll in this foam testing machine is such as to drag glue through the gap or slit and around into the upper part of the hopper, thus causing the glue in the hopper to entrain air as it rolls in contact with the revolving roll. Thus, the machine accurately tested the glue compositions as to their foaming tendency under production conditions, since a closely similar hopper feeding mechanism and steel roll driven at substantially the same speed are employed in production in the spreading of glue during the manufacture of a laminated product such as plywood.

As an accurate measure of the foaming tendency of a given solution, it is to be considered that the specific gravity of the solution provides an accurate measure of such foaming tendency, or more accurately the degree of air entrainment in the composition. A normal glue solution will usually have a specific gravity at 70° F. of between 1.00 and 1.15 when freshly mixed. After a given glue solution was subjected to the foaming action for ex-

tended periods, the specific gravity was measured and the difference in specific gravity between the initial and foamed glue provided an accurate measure of the foaming tendency of the glue.

As previously indicated, the following examples are merely illustrative of certain specific embodiments of the present invention and discovery, and are not to be construed as restricting the scope thereof.

Example 1

In this and the following examples, unless otherwise indicated, the specific anti-foaming composition tested was employed in the amount of 16 parts by weight per 400 parts of soybean flour. In Example 1, the specific anti-foaming composition representative of the present invention and discovery which was tested was compounded by mixing 20 parts di-iso-butyl carbinol, 1.5 parts stearic acid and 95 parts diesel oil as an extender. The specific gravity of the glue composition including the anti-foaming composition, measured at 70° F., after initial mixing was 1.06. After 10 minutes of testing on the foam machine the specific gravity was 1.02, after 20 minutes was 0.99 and after 30 minutes was 0.90.

Example 2

As a variation of the above anti-foaming composition, 21 parts of the anti-foaming composition was used in the mix rather than 16 parts and an additional 120 parts of water containing 20 parts of sodium pentachlorophenate were added after the sodium silicate addition with an additional stir period of two minutes. With this slightly modified constituency and procedure, the initial specific gravity of the mixed glue was 1.06. After 10 minutes of testing on the foam machine the specific gravity was 0.96, after 20 minutes was 0.91, and after 30 minutes was 0.85.

Glue solutions incorporating sodium pentachlorophenate account for at least 90% of the glue used commercially in the plywood industry, since it has proven to be an effective preservative in protein-base glues in preventing microbial decomposition of the glue and delamination of the plywood. Use of sodium pentachlorophenate, however, increases the tendency of a given glue solution to foam, and its almost universal use materially increases the importance of the present invention in providing an effective anti-foaming agent even in the presence of sodium pentachlorophenate, as demonstrated by the above example.

Example 3

Since di-iso-butyl carbinol is typical of the liquid alcohols employed as an ingredient in anti-foaming agents herein contemplated, combinations therewith of various saturated fatty acids and nonsaturated acids to demonstate this feature of the invention are considered appropriate. Accordingly, in Example 3 myristic acid was substituted in the same proportion for stearic acid in Example 1, with the following results. The initial specific gravity of the glue, mixed at 70° F., was 1.02. After 10 minutes of testing on the foam machine the specific gravity was 0.98, after 20 minutes was 0.95, and after 30 minutes was 0.95.

Example 4

Same as Example 1 except that behenic acid was substituted for stearic acid in the same proportion, with the following results. Initial specific gravity at 70° F. was 1.06. After 10 minutes of testing on the foam machine the specific gravity was 1.03, after 20 minutes was 0.99, and after 30 minutes was 0.94.

Example 5

To demonstrate the nonapplicability of the nonsaturated acids in practice of the present invention, this example substituted oleic acid for stearic acid in the same proportion as undertaken in Example 1, with the following results. The initial specific gravity measured at 70° F. was 1.00. After 10 minutes of testing on the foam machine the specific gravity was 0.84, after 20 minutes was 0.81, and after 30 minutes was 0.78.

Example 6

A further variation illustrating the nonapplicability of unsaturated acids to the present invention was demonstrated by the following example, wherein the stearic acid of Example 1 had substituted therefor linoleic acid in the same proportion. Under these circumstances, the specific gravity measured at 70° F. after the initial mix was 0.99. After 10 minutes of testing on the foam machine the specific gravity was 0.91, after 20 minutes was 0.80, and after 30 minutes was 0.70.

Example 7

An anti-foaming composition according to the present invention was made by mixing 20 parts amyl alcohol, 1.5 parts stearic acid and 95 parts diesel oil, which anti-foaming composition was tested exactly as in Example 2, with the following results. The initial specific gravity measured at 70° F. of the mixed glue was 1.04. After 10 minutes of testing on the foaming machine the specific gravity was 0.90, after 20 minutes was 0.86, and after 30 minutes was 0.85.

Example 8

A modified liquid defoamer composition was made by mixing 19 parts pine oil, 2.5 parts stearic acid and 95 parts diesel oil, which anti-foaming composition was tested exactly as in Example 1. The specific gravity of the initial mix glue was 1.07. After 10 minutes of testing on the foam machine the specific gravity was 1.02, after 20 minutes was 0.99, and after 30 minutes was 0.92.

Example 9

A liquid anti-foaming composition was prepared by dissolving together at about 120° F. the following: stearic acid 1 part, pine oil 2 parts, naphthenic-acid-tri-ethylene-tetramine condensation product (100 parts naphthenic acid and 15 parts tri-ethylene tetramine, prepared as indicated above) 5 parts, and diesel oil 22 parts. This mixture demonstrated a viscosity only slightly more than the viscosity of diesel oil and does not crystallize or sludge out under ordinary temperature conditions as encountered in storage. Further, the solution is anti-corrosive and may be stored for a year or more in steel drums, and has proved exceptionally effective. When mixed with the glue according to Example 1, in the amount of 16 parts per 400 parts of soybean flour, this anti-foaming solution demonstrated a specific gravity after initial mixing thereof of 1.07 at 70° F., and after 10 minutes on the foam machine the mix had a specific gravity of 1.00. After 20 minutes on the foam machine the specific gravity was 0.98, and after 30 minutes on the foam machine the specific gravity was 0.95.

Example 10

The anti-foaming composition tested in this example was prepared according to the following formulation; stearic acid 1 part, pine oil 2 parts, stearic-acid-propylene-diamine condensation product (stearic acid, triple pressed, 57 parts and propylene diamine 3.7 parts), 5 parts, and diesel oil 37 parts. This solution was stable and did not precipitate when stored at 40° F.

This anti-foaming composition was tested exactly as in Example 1. The specific gravity measured at 70° F. of the mixed glue was 1.06. After 10 minutes on the foam machine the specific gravity was 1.02, after 20 minutes the specific gravity was 0.94, and after 30 minutes was 0.88.

Example 11

An anti-foaming agent according to the present invention was prepared by mixing 3 parts stearic acid, 12 parts tri-butoxy-ethyl-phosphate and 200 parts diesel oil, which anti-foaming agent was tested exactly as in Example 2. The specific gravity measured at 70° F. of the glue after

initial mixing was 1.06. After 10 minutes of testing on the foam machine the specific gravity was 0.98, after 20 minutes was 0.91, and after 30 minutes was 0.85.

Example 12

An anti-foaming agent according to the present invention was prepared by mixing myristic acid 1 part, pine oil 2 parts, naphthenic-acid-tri-ethylene tetramine condensation product (naphthenic acid 100 parts, and tri-ethylene tetramine 15 parts) 5 parts, and diesel oil 32 parts. When tested exactly as in Example 1, the glue had an initial specific gravity of 1.06, after 10 minutes on the foam machine demonstrated a specific gravity of 1.04, after 20 minutes demonstrated a specific gravity of 1.02, and after 30 minutes demonstrated a specific gravity of 1.00.

Example 13

A liquid anti-foaming agent was prepared by mixing arachitic acid 1 part, pine oil 2 parts, condensation product of naphthenic acid and tri-ethylene tetramine as in Example 12, 5 parts, diesel oil 32 parts. When tested as in Example 1, the glue mix had an initial specific gravity of 1.07 at 70° F., after 10 minutes the specific gravity was 1.04, after 20 minutes was 1.00, and after 30 minutes was 0.95.

Example 14

A liquid anti-foaming agent according to the present invention was prepared by mixing 12 parts stearic acid, 12 parts tri-butoxy ethyl phosphate, 6 parts naphthenic-acid-tri-ethylene-tetramine condensation product (as in Examples 12 and 13) and 163 parts diesel oil. When tested exactly as in Example 1, the glue mix had an initial specific gravity at 70° F. of 1.08, after 10 mintues on the foam machine a specific gravity of 1.06, after 20 minutes the specific gravity was 1.03, and after 30 minutes was 0.99.

Example 15

A liquid anti-foaming agent according to the present invention was prepared by mixing 12 parts tributyl phosphate, 16 parts stearic acid, and 200 parts kerosene. When tested exactly as in Example 1, the glue mix had an initial specific gravity at 70° F. of 1.07, after 10 minutes on the foam machine a specific gravity of 1.01, after 20 minutes a specific gravity of 0.95, and after 30 minutes a specific gravity of 0.88.

Example 16

A liquid anti-foaming agent according to the present invention was prepared by mixing 12 parts di-amyl butyl phosphonate, 12 parts butanol-1, 3 parts stearic acid, and 200 parts light petrolatum. When tested exactly as in Example 1, the glue mix had an initial specific gravity at 70° F. of 1.08, after 10 minutes on the foam machine a specific gravity of 1.00, after 20 minutes a specific gravity of 0.95, and after 30 minutes a specific gravity of 0.86.

Example 17

A liquid anti-foaming agent according to the present invention was prepared by mixing a condensation product contemplated by the present invention (oleic acid 100 parts and tri-ethylene tetramine 15 parts) 5 parts, pine oil 2 parts, stearic acid 1 part, and diesel oil 32 parts. When tested exactly as in Example 1, the glue mix of this example had an initial specific gravity at 70° F. of 1.04, after 10 minutes on the foam machine a specific gravity of 0.97, after 20 minutes a specific gravity of 0.90, and after 30 minutes a specific gravity of 0.85.

Example 18

It is not necessary that the liquid defoamer composition, such as in Example 1, be added to the water prior to the addition of the protein material to be wet mixed. Any portion of the liquid defoamer composition may be incorporated with the protein material in substantially a dry mixing operation prior to the water mixing step. This is particularly attractive in defoaming soybean flour because today most soybeans are extracted free of oil by solvent extraction processes and it is a comparatively simple procedure to introduce my defoamer in whole or in part using the same equipment used to extract the soybean oil. Thus, soybean flakes may be extracted with hexane as a solvent to remove the soybean oil and then treated with a solution of a saturated fatty acid having a molecular weight of at least 228, in sufficient concentration in a suitable organic solvent to allow the retention of from 0.01% to about 0.2% by weight of the saturated fatty acid. For example, 100 parts of dry comminuted soybeans were extracted with n-hexane in conventional manner until oil free. Then after the n-hexane was removed from the soybean flakes, the flakes were treated at room temperature with a solution of 1.5 parts of stearic acid in 400 parts of commercial ethyl alcohol. The excess alcohol solution was removed and 40 parts of solution remained. The flakes were then dried with full recovery of the ethyl alcohol, leaving about 0.15 parts of stearic acid per 100 parts of flakes distributed throughout the flakes. The flakes were then ground to flour and used as an adhesive. In preparing an anti-foaming solution from this material, 4 parts of a mixture of diesel oil, pine oil and naphthenic-acid-tri-ethylene tetramine condensation product in the same proportions as in Example 9 were used.

This anti-foaming solution produced a specific gravity after initial mixing thereof, at 70° F. of 1.08, after 10 minutes on the foam machine the specific gravity was 0.97, after 20 minutes it was 0.91, and after 30 minutes it was 0.85.

It will be readily understood by those skilled in the art that a solvent extracted soybean meal or flour characterized by absence of vegetable oils and treated with a saturated fatty acid has advantageous utility in the formulation of a defoamed protein-base adhesive solution according to the present invention, and has the further advantageous characteristic that such treatment does not destroy the utility of the soybean meal or flour for other uses, as in food for human or animal consumption. Further, the pre-addition of the saturated fatty acid to the soybean meal or flour in dry form effectively serves to minimize dusting in a product of commerce having a wide variety of uses and customarily handled, shipped and stored in dry form, all without adverse effect on its physical appearance, its essentially dry character, or its edibility. Thus, soybean meal or flour used in the formulation of adhesives may have the saturated fatty acid pre-mixed therewith at the point of manufacture and thus simplify the formulation of a defoamer addition agent added at the situs of use, with the further advantage of dust minimization during handling and shipping and without limitation or detriment as to other uses of the meal or flour (i.e. meal or flour destined for adhesive use need not be specially prepared or processed at the mill, as is often the case in conventional practice).

The foregoing Example 18 is just one example of combining a part of the defoamer composition in a dry mix with the protein-base ingredient. It is not necessary that the fatty acid be added in solution since a dry blend of finely ground fatty acid and soybean flakes or flour may be utilized or the fatty acid may be sprayed into the soybean material. Furthermore, a mixture of a liquid alcohol such as di-iso-butyl alcohol or the like, can be added with a fatty acid such as stearic acid to an extracted soybean meal in a dry blender and produce a mixture which is for all practical purposes dry to the touch even though up to 10% by weight of total liquids may be present. Such a material is useful as an adhesive base when mixed with water and suitable alkalis according to known procedures.

While the foregoing examples have been limited to demonstrating the relative efficacy of various anti-foaming compositions according to the present invention and various such other compounds and compositions for com-

parison purposes, as utilized in soybean protein adhesive glue solutions, it is to be understood that these examples are merely illustrative of the invention and it will be apparent that in fields where comparable solutions are encountered, the anti-foaming agents and foam abatement procedures set forth and illustrated provide advantages and are effective within the scope of the present invention.

Based on the foregoing examples and other considerations such as economy and relative effectiveness in use on a commercial scale, it has been determined that the approximate proportions of the various components for formulating anti-foaming agents having desirable characteristics according to the present invention proportionate to the weight of the protein-base meal of flour in dry form and exclusive of the extender ingredient, can be established as follows:

	Percent	
	From	To
Saturated aliphatic acid	0.06	0.28
And an effective amount of one or more of the following:		
Liquid monohydric alcohol having at least four carbon atoms per molecule	0	0.68
Tri-alkyl phosphate and/or tri-alkyl phosphonate	0	0.20
Tri-alkoxy phosphate	0	0.29
Substituted amine surface active agent	0	0.66

In general and as a practical matter the relative proportion (i.e. concentration) of the saturated aliphatic acid ingredient is limited by the solubility of the particular saturated fatty acid in the particular extender (and liquid alcohol, if present) at the minimum temperature to be encountered during storage of the foam inhibitor. Of course, if the glue solution is prepared directly before use in production of a laminated or similar product and without being stored, such minimum temperature requirement is less severe and a higher proportion of the saturated fatty acid can be employed if desired. It has been further determined that the relative weight of the above components and the extender employed in a given solution, as contemplated by the present invention, can advantageously be varied in range with the relative proportion of said components being directly related to the proportion of extender or spreading agent used in the anti-foaming agent in a percentage from about 7% to about 27% with about 18% being preferred. Obviously, in many applications an even higher concentration of said components in the extender will perform a very effective defoaming action, but such higher relative concentrations are normally not feasible as the increase in expense, and loss in spreadability in the aqueous solution, do not warrant the increased concentration of the active ingredients of the anti-foaming agent.

Other variations and modified formulations will readily occur to those skilled in the art, within the scope of the following claims.

This application is a continuation-in-part of my copending application Ser. No. 603,176, filed August 9, 1956, entitled "Anti-Foaming Agents for Alkaline Aqueous Protein Solution and the Like," which is in turn a continuation-in-part of my patent application Ser. No. 488,436, entitled "Defoamer Material," filed February 15, 1955, and which is also in turn a continuation-in-part of my continuation application Ser. No. 559,134, entitled "Defoamer Material," filed January 16, 1956, all of the said prior applications being now abandoned.

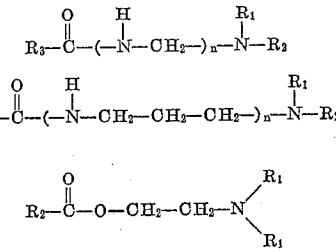
What is claimed is:

1. A dust-inhibited composition of matter which is edible yet of specially advantageous utility as to improving the effectiveness of an anti-foaming agent compounded therewith in the formulation of a defoamed aqueous adhesive solution, said composition of matter consisting essentially of solvent extracted ground soybean material in essentially dry state, with about 0.01% to about 0.2% by weight of uncombined saturated fatty acid admixed therewith, the saturated fatty acid having a molecular weight of at least 228.

2. A composition of matter according to claim 1, wherein said saturated fatty acid is selected from the group consisting of myristic, palmitic, stearic, arachitic, behenic acids and the higher homologues thereof, and mixtures thereof.

3. A composition of matter according to claim 1, wherein said saturated fatty acid is stearic acid.

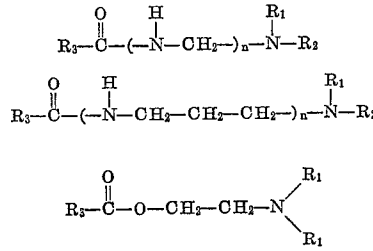
4. A foam inhibitor for proteinaceous adhesive solutions, consisting essentially of a substantially water insoluble solution of uncombined saturated fatty acid of molecular weight of at least 228, such acid having present therewith a constituent selected from the following group of foam inhibiting compounds, and mixtures thereof: monohydric liquid alcohols; tri-alkyl phosphates; tri-alkyl phosphonates; tri-alkoxy phosphates, and substituted amine surface active agents conforming to one of the following formulas:



or

where R_1 and R_2 are an H, or an alkyl, aralkyl, or hydroxy substituted alkyl group, R_3 is an alkyl, alkenyl, naphthenyl, or aralkyl group having at least 4 carbon atoms, and n is 1, 2, 3, or 4.

5. In composition with an aqueous proteinaceous adhesive solution, a foam inhibitor consisting essentially of a substantially water insoluble solution of uncombined saturated fatty acid of molecular weight of at least 228, said acid having present therewith a constituent selected from the following group of foam inhibiting compounds, and mixtures thereof: monohydric liquid alcohols; tri-alkyl phosphates; tri-alkyl phosphonates; tri-alkoxy phosphates, and substituted amine surface active agents conforming to one of the following formulas:



or

where R_1 and R_2 are an H, or an alkyl, aralkyl, or hydroxy substituted alkyl group, R_3 is an alkyl, alkenyl, naphthenyl, or aralkyl group having at least 4 carbon atoms, and n is 1, 2, 3 or 4.

6. A foam inhibited composition according to claim 5, wheren said aqueous proteinaceous adhesive solution contains a chlorophenate as a preservative.

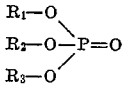
7. A foam inhibitor according to claim 4 wherein said saturated fatty acid is selected from the group consisting of myristic, palmitic, stearic, arachitic, behenic acids and the higher homologues thereof, and mixtures thereof.

8. A foam inhibitor according to claim 7, wherein said saturated fatty acid is stearic acid.

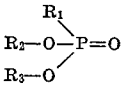
9. A foam inhibitor according to claim 4 wherein said alcohol is selected from the group consisting of monohydric, aliphatic, cyclic, non-aromatic primary, secondary and tertiary carbinols having a liquid form at room temperature, having at least four carbon atoms, and having a solubility in water of not more than about nine parts per 100 at 15° C.

10. A foam inhibitor according to claim 9, wherein said monohydric alcohol is selected from the group consisting of di-isobutyl carbinol, amyl alcohol, butanol-1, and pine oil.

11. A foam inhibitor according to claim 4 including a phosphorous-containing compound selected from the group consisting of tri-alkyl phosphtae, tri-alkyl phosphonate, and tri-alkoxy phosphate, conforming to one of the following formulas:



a phosphate ester where R_1, R_2, R_3 are alkyl or alkoxy groups, or



an alkyl phosphonate where R_1 is an alkyl group, and R_2 and R_3 are alkyl or aralkyl groups.

12. A foam inhibitor according to claim 4 wherein said substituted amine surface active agent is a reaction product selected from the group consisting of the reaction product of palmitic acid and ethylene diamine, the reaction product of stearic acid and propylene diamine, the reaction product of oleic acid and diethylene triamine, the reaction product of naphthenic acid and tri-ethylene tetramine, the reaction product of pelargonic acid and tetra-ethylene pentamine, the reaction product of phenylpropionic acid and di-ethylene triamine, the reaction product of stearic acid and di-methyl ethanolamine, and the reaction products of any of the above acids with any of the above amines.

13. A foam inhibitor according to claim 4 wherein the solvent vehicle of such solution is a hydrocarbon diluent substantially insoluble in water and having a kauri-butanol value of not more than 40, the said hydrocarbon diluent functioning of itself as a non-deleterious foam inhibitor.

14. A foam inhibitor according to claim 13, wherein said solvent vehicle is a petroleum distillate selected from the group consisting of kerosene, fuel oil, diesel oil and light petrolatum.

15. A foam inhibited composition according to claim 5 wherein said saturated fatty acid is selected from the group consisting of myristic, palmitic, stearic, arachitic, behenic acids and the higher homologues thereof, and mixtures thereof.

16. A foam inhibited composition according to claim 15, wherein said saturated fatty acid is stearic acid.

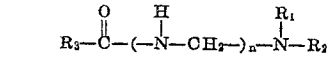
17. A foam inhibited composition according to claim 5, wherein the solvent vehicle of such solution is a hydrocarbon diluent substantially insoluble in water and having a kauri-butanol value of not more than 40, the said hydrocarbon diluent functioning of itself as a non-deleterious foam inhibitor.

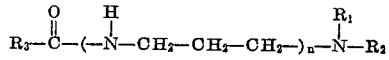
18. A foam inhibited composition according to claim 17, wherein said solvent vehicle is a petroleum distillate selected from the group consisting of kerosene, fuel oil, diesel oil and light petrolatum.

19. An aqueous adhesive solution comprising an anti-foaming agent and an proteinaceous adhesive forming material, wherein said anti-foaming agent consists essentially of a substantially water insoluble solution wherein is present the following compositions and range of proportions with respect to the dry weight of said adhesive forming material:

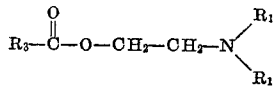
	Percent
Saturated aliphatic acid having a molecular weight of at least 228	0.06 to 0.28
And at least one of the following:	
Liquid monohydric alcohol having at least four carbon atoms per molecule	0 to 0.68
Tri-alkyl phosphate and/or tri-alkyl phosphonate	0 to 0.20
Tri-alkoxy phosphate	0 to 0.29
Substituted amine surface active agent	0 to 0.66

said substituted amine surface active agent conforming to one of the following formulas:





or



where R_1 and R_2 are an H, or an alkyl, aralkyl, or hydroxy substituted alkyl group, R_3 is an alkyl, alkenyl, naphtenyl, or aralkyl group having at least 4 carbon atoms, and n is 1, 2, 3, or 4.

20. A solution according to claim 14, further having a composition therewith a water insoluble hydrocarbon extender for said anti-foaming agent, the proportion of said anti-foaming agent with respect to said extender being from about 7% to about 27%.

21. A solution according to claim 20, wherein said anti-foaming agent is present in an amount of about 18% by weight of said solution.

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