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PROTEOLYTIC BATING COMPOSITION

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This invention relates to the art of treating hides and skins, and may be considered as relating to the art of bating hides and skins.

Before hides and skins are tanned or converted into commercial leather they are subjected to a number of preparatory processes. There are, of course, various routines followed in these intermediate operations. According to one commonly used procedure, the skins or hides are given a preliminary soak and then subjected to a process for loosening the hair so that it can be readily removed. One of the common methods of hair loosening is to subject the skins or hides to a lime or other alkaline bath, with or without the addition of other chemicals. The loosened hair is then removed mechanically. After removal of the hair, the skins are turned over and scraped with knives to remove as much of the adipose tissue as can be removed in that manner. Then the skins are bated, this step being more fully referred to hereinafter. Following bating, the scud is removed by machine or by washing. There are other intermediate steps prior to tanning, but they require no comment here.

There are, as stated, other modes of intermediate treatment. The present invention is directed more particularly to the general procedure above outlined but is applicable to other procedures, as will be more apparent from the ensuing description.

As a result of the lime or other alkaline treatment, the fibres of the hides or skins have more or less resiliency or elasticity. In addition, the treatment with lime or with any other alkali, such as caustic soda, or with alkaline salts, causes a swelling of the hides or skins. Before the hides or skins can be tanned, they must be "brought down" or "reduced," particularly in the production of light and soft leathers, in order to remove this elastic or resilient condition, render the hides or skins soft, supple and flaccid, and to remove the plumpness caused by the alkaline swelling.

Further, and particularly in the case of finer upper leathers, the dirt and "scud" still contained in the hides or skins after the alkaline hair-loosening treatment must be loosened so that it can be readily removed to as full extent as possible by washing or by pressing or scraping. This scud consists mainly of hair roots, deep seated fine hairs, parts or fragments of the so-called sweat or tallow glands, epidermal matter which reaches more or less deeply into the grain layer, pigment cells and fatty substances, often of cholesterin nature. The scud, when removed, is a more or less darkish thick mass of somewhat

gluey consistency. The thorough removal of the scud is of particular importance where it is desired that the final leather have a clear and uniform color since, without thorough removal, such leather cannot be attained.

The earliest known method of treatment for "reducing" etc., was to subject the hides or skins to the action of a bath formed from animal manure. This process became known as "puering." Such process, however, is subject to various objections and disadvantages. For example, it is disagreeable. It also involves a more or less violent fermentation with the formation of various gases and other compounds of organic or inorganic nature, including CO₂, and because of such fermentation, there is considerable danger of damage to the hides or skins by reason of bacterial attack. Moreover, the process is exceedingly difficult to control.

For these and perhaps other reasons, this method has been largely superseded by the use of various proteolytic enzyme preparations generally known as "bates." Most of these artificial bates are ordinarily used in connection with some neutralizing agent such as inorganic or organic acids, acid salts and, more particularly, ammonium salts. The action of the proteolytic enzyme in this bating process is presumably a dissolving or peptizing action on different protein constituents of the skins.

In the case of the production of sole leather, many tanners are satisfied with more or less "neutralization" or partial removal of the alkalinity of the hides to a pH ranging from slight acidity to about 10, using only neutralizing agents such as mentioned above with little or no proteolytic enzyme. But in the case of leathers which should be supple and flaccid, and where the final color of the leather after dyeing should be clear and uniform, for example, calf, kid, and sheep leathers, the skins are ordinarily bated or puered.

While the term "puering" was formerly applied to dog manure baths and the term "bating" to the use of pigeon manure baths and artificial bates of enzymatic nature, the term "bating" is now more or less commonly accepted as referring to any treatment for "reducing" hides and skins, rendering them soft, etc. In that sense, the process of the present invention may be said to be an improvement in the art of bating.

In addition to the necessity for "reducing" the skins and hides, it is also desirable that the adipose tissue be thoroughly loosened, at least in the case of the preparation of finer leathers.

The mechanical removal of the adipose tissue from the flesh side of the skins, as above referred to, ordinarily does not remove all such tissue. There remains what may be termed a residue, more or less in the form of a tight membrane. While the matter is of relatively little importance in the case of heavy leathers, it is difficult, if not impossible, to produce proper leathers of the finer types if this residue is left in its original condition.

It has been found, however, that this residue need not be entirely removed and that the difficulties referred to, can, to a greater or less extent, be avoided if such adipose tissue is rendered loose. A proper bating treatment causes more or less loosening of this adipose tissue residue. Ordinarily, therefore, such loosening is relied upon and skins and hides are seldom treated after bating for complete removal of the adipose tissue. As far as this feature is concerned, it will be seen that the looser such tissue after bating, the more satisfactory the bating is considered. A test commonly applied is to ascertain how easily the remaining adipose tissue can be scraped off with the thumb nail after the bating treatment. The more easily this can be done, the more successful is the bating in this respect.

It is an object of the present invention to provide an improved method of treating hides and skins by which the hides and skins may be "brought down" and "reduced" and rendered properly soft, supple and flaccid and by which the scud and adipose tissue may be more thoroughly loosened than with previously known methods, whereby clearer skins may be obtained which take a dye more uniformly and can be converted into final leather of more uniform and clearer color. Other objects and advantages will be apparent from the following description.

According to the invention in its entirety, we subject the skins or hides to the action of an aqueous bath containing one or more sulphur compounds of the class in which sulphur is combined with hydrogen or with hydrocarbon or substituted hydrocarbon radicles of aromatic or aliphatic origin. The members of this group, in addition to hydrogen sulphide and the hydrogen polysulphides, may be considered as derivatives of hydrogen sulphide or polysulphides by replacement of one or both hydrogens by aliphatic or aromatic radicles or by an amine or ammonia group or any aliphatic or aromatic amine or by replacement of one hydrogen by an alkali metal or alkaline earth metal.

If the general preparatory procedure above outlined is followed, the skins and hides are subjected to the bath described following the de-hairing operation, whether with or without an intervening wash. If other procedures are followed, for example, one in which the hides or skins are to be "reduced" before dehairing, then the bath treatment is applied after the alkaline swelling and before dehairing.

We have found that when skins or hides are immersed, under suitable conditions, in an aqueous bath containing a compound or mixture of compounds of the class referred to, and having an initial pH value lower than that of the limed or alkaline treated skins, surprising and unexpected results are obtained. Not only are the skins or hides rendered soft, supple and flaccid, but, in addition, the dirt and scud and the adipose tissue are thoroughly loosened.

While the mechanism of the action obtained is not entirely known, it appears possible that the

sulphur compound combines with the materials present, more or less alkaline in character, and acts to reduce the alkalinity of the skins or hides, and the formed sulphur compounds influence, dissolve or peptise certain protein constituents of the skins or hides to make them soft and supple.

Whatever may be the explanation, the fact remains that the treatment described attains results in many respects superior, and in no respect inferior, to the results obtained by previously known treatments.

Compared to "neutralization" alone, particularly to cases where skins are only partly neutralized to a pH of about 10 to 11.5, the results are greatly superior in every respect. With neutralization alone, the skins or hides, while partly "reduced," are hard feeling and the scud and adipose tissue are only partly loosened. But with the treatment of the present invention, the skins are well "reduced," are soft and supple and the scud and adipose tissue are thoroughly loosened.

Compared with previously known bating and puering methods, improved results are also obtained. The skins and hides treated as described may be rendered soft and supple to a degree as great as or greater than in the case of previously known methods. Moreover, the scud and adipose tissue may be loosened more thoroughly than with previously known methods. As a result, it is possible to obtain final leather of good quality having a clear and uniform color to a high degree.

The treatment of the present invention is particularly advantageous as compared with puering with animal manures since not only are improved results obtained but the objections and disadvantages of puers above referred to are avoided.

In carrying out the treatment above referred to, while the skins are usually subjected to a prior water wash, washing is not essential.

While the amount of water in the aqueous bath may vary within a considerable range, for example, from 1 to 12 parts of water to 1 part skins, based on limed weight, we have found that a water-to-skin ratio of from 2:1 to 6:1 gives satisfactory results.

The temperature of the bath may also vary, for example, from 50° to 120° F. However, a temperature of from 70° to 100° F. has been found to be satisfactory. It is not necessary to maintain any specific starting temperature but the temperature should be maintained above the minimum of the range.

While the initial pH of the bath may vary from a slight acidity of 5 up the alkaline range to about 11.5, a range of from about 6 to about 10.6 normally gives what are now considered the best results. In referring to the initial pH value, we mean, unless otherwise specified, the pH value at the time or shortly after the time when skins or hides are immersed in the bath.

The duration of treatment in the bath depends largely on the action desired and the type of skins or hides being treated. For example, heavy hides for sole leather take a relatively short treatment whereas goat-skins for finer leather are ordinarily treated at least over night. Under practically no circumstances is a treatment over 24 hours required.

The amount of sulphur compound used may also vary within a considerable range and depends on various factors. In this connection, it

is to be understood that two actions are involved in obtaining the desired results: (1) the specific action of the sulphur compound as such; and (2) a neutralizing action. The sulphur compound itself may perform both functions but need not necessarily do so. That is to say, it may be desirable to supplement the action of the sulphur compound with what may be termed a "normal" neutralizing agent such as ammonium salts, e. g. sulphate, chloride or carbonate, inorganic or organic acids or acid salts. In fact, since, as we have found, only a small amount of sulphur compound is necessary for the desired specific sulphur action, we ordinarily do use such "normal" neutralizing agents.

It is to be noted in this connection that if a separate neutralizing agent is to be used, it may be added with the sulphur compound or prior or subsequent to such addition.

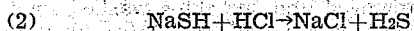
Referring further to proportions of materials, and taking hydrogen sulphide as an example of the sulphur compound to be used, the proportional amount may vary within a wide range, for example, from 0.001 pound to 10 pounds per 100 pounds of skins or hides (unhaired weight). Since hydrogen sulphide is a weak acid, the larger proportions are indicated when that compound is relied upon for both the specific sulphur action and the neutralizing action, the smaller proportions being indicated when a separate neutralizing agent is used. In the latter case, a range of from 0.01 pound to 1 pound of hydrogen sulphide per 100 pounds of skins or hides has been found to give satisfactory results.

When sulphur compounds other than hydrogen sulphide are used, the relative amounts may vary within a range of like order, the proportion used depending, at least in part, on the neutralizing power of the sulphur compound and the presence or absence of separate neutralizing agents.

The sulphur compound or compounds need not necessarily be added to the bath as such. They may be generated in the bath if desired. Such procedure is particularly convenient when it is desired to use hydrogen sulphide since it avoids the more or less obvious disadvantages of storing and handling H_2S gas. In other cases, the starting materials for generating a given compound may be more available or more convenient than the compound itself.

As an example of such generation of compounds in the bath itself, hydrogen sulphide (H_2S), sodium sulphhydrate ($NaSH$) or combinations of these compounds may be generated in the bath by adding to the water sodium sulphide and a suitable acid.

When, for example, sodium sulphide and hydrochloric acid are brought together, two reactions are, or may be involved:



Since both hydrogen sulphide and sodium sulphhydrate (sodium hydrosulphide) are capable of performing the specific sulphur action here involved, it does not matter, broadly speaking, to what extent, if any, Equation 2 is realized. However, since sodium sulphhydrate is less active than hydrogen sulphide, in carrying out the invention to what is now considered the best advantage, we so proportion the starting materials that there is enough HCl in excess of the requirements of Equation 1 to transform at least a substantial

portion of the $NaSH$ into H_2S in accordance with Equation 2.

Other sulphides and acids may be used in generating the desired sulphur compounds in the bath by reactions of the general type above referred to. For example, the sulphides of the alkali-alkaline earth groups, with which is grouped, at least theoretically, ammonium sulphide, may be used. As further examples of acids, boric acid and carbonic acid may be used.

As a further example of the generation of sulphur compounds along the lines described, when calcium sulphide is added to a fermenting puer, the CO_2 evolved in the bath reacts with the calcium sulphide and reactions analogous to those mentioned may take place:



When the sulphur compound that is to be used is something other than hydrogen sulphide, it may be generated in the bath by a reaction of a type exemplified by the following:



In connection with Equation 5 it is recognized that ammonium sulphide dissociates into NH_4SH and ammonia.

In order to obtain what are now considered optimum results, we supplement the action of the sulphur compound by the action of suitable proteolytic enzymes. Such enzymatic products may be derived from various sources, for example, pancreas glands or preparations containing the proteases of various plants or molds or other micro-organism such for example, as bacterial proteases. It is to be understood, however, that the enzymes used should be such that they are active in the pH range prevailing and such that their activity is not seriously reduced by the particular sulphur compound used or by the products formed in the bath.

If an enzymatic preparation is used in conjunction with the sulphur compound it may be added either before or with or after the addition of the sulphur compound and in such amounts as are generally used in enzymatic bating.

The invention in its entirety includes the provision of a composition of matter which may be termed a bating mixture, suitable for carrying out the treatment above described, and which may be supplied to tanneries ready for addition to the bath. Such a mixture, in dry form, may conveniently comprise a pancreatic or bacterial enzyme absorbed on wood flour; a relatively insoluble sulphide and a neutralizing agent.

For the neutralizing agent, ammonium salts, such as chlorides or sulphates, or boric acid may be used. For the sulphide, we have found, for example, that calcium sulphide gives suitable and satisfactory results. Being largely insoluble and non-hygroscopic it does not substantially upset the stability of the dry bating mixture and there is substantially no danger of destruction of the enzymes by decomposition of the ammonium salts or otherwise.

Such a mixture is of particular advantage in that it may be compounded at the source and supplied commercially to tanneries as a bating mixture ready for use. In this manner, the relative proportions may be controlled or standardized, leaving nothing to the tanner except to measure out the prescribed amount of the mixture according to the weight of the particular batch of hides or skins to be treated. Being in

dry form, the mixture is convenient to store and ship and is itself stable in the sense that substantially no reaction takes place between the ingredients prior to addition to the water of the bath.

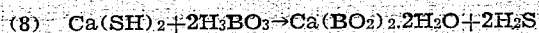
While the proportions of the starting materials in a bate mixture of the character described may vary within a considerable range, we have found that satisfactory results are obtained with the following approximate proportions by weight: Sulphide, e. g., calcium sulphide, 5-10%; neutralizer, e. g., ammonium salt, 60-80%; enzymatic material absorbed on wood flour by balance.

When a mixture including calcium sulphide and ammonium chloride, for example, is added to the water of the bath, ammonium sulphide is formed by reaction as represented by the following equation:



the ammonium sulphide dissociating into NH_4HS and ammonia.

If boric acid is used instead of an ammonium salt, the following double or continued reactions are or may be involved:



It will be understood that both an ammonium salt and boric acid may be used for neutralizing.

It is to be understood that, if desired, either the sulphide or the neutralizing agent may be omitted from the commercial mixture above referred to and added to the bath independently. Such procedure, however, obviously detracts somewhat from the full advantages above described.

In the various reactions above referred to, the resulting sodium chloride, calcium carbonate, calcium chloride and calcium borate are neutral and inert as far as the treatment bath is concerned. It is also to be understood that the various reactions above set forth are explanatory only and that additional or more complicated reactions may occur.

In many cases, the hides or skins treated as above described are ready for pickling, tanning or other subsequent operations. If, for any reason, it is desired that the skins be free from the sulphur compounds referred to or the salts or other compounds formed during the process, the treated skins or hides may be washed or subjected to mechanical operation for complete removal of the loosened scud, such as slating, prior to subsequent operations such as pickling or tanning.

If desired, the treatment with a sulphur compound as above described may be followed by the usual bating or puering operation or by the usual neutralization. Such additional and supplemental treatment is of particular advantage if it is desired that the skins or hides should be brought down to a pH of 8 or 9 or lower.

The following more specific procedures, found to have given suitable and satisfactory results, are cited by way of example. The skin weights given are "white weight," i. e. weight after de-hairing and fleshing. Sufficient agitation to obtain a thorough mix is assumed. Where the use of a disinfectant is cited, any suitable disinfectant may be used, for example, that disclosed in United States Patent 1,985,267. Where the use of enzymatic preparations absorbed on wood flour is specified, the weight given includes both the absorbed and absorbing material. After completion of the steps set forth, the skins are ready for

pickling, tanning, etc., in accordance with known practice.

As a result of these procedures, the skins are soft, supple and flaccid and the scud, dirt and adipose tissue are thoroughly loosened, the latter being loose enough to be easily scraped off by the thumb nail in a test of the character above referred to. Assuming proper tanning and other subsequent operations, the treatments described result in clear skins which can take a dye uniformly and which make possible a final leather of outstanding uniformity and clearness of color.

Example 1

3.3 pounds hydrogen sulphide (H_2S), obtained by neutralizing the corresponding amount of sodium sulphide with hydrochloric acid, were dissolved in 4500 pounds water at 96° F. Into this bath 1155 pounds calf skins were placed and left over night with occasional stirring. The initial pH of the bath was 6.5 and the final pH 10.1.

Example 2

1350 pounds kid skins were put in a bath consisting of 5400 pounds water to which was added 6.7 pounds fused sodium sulphide (approximately 62% Na_2S) and 43 pounds diluted hydrochloric acid (7.3% HCl). Then there was added 2.6 pounds of an enzymatic pancreas preparation absorbed on wood flour. The skins were left in this bath over night. The pH before adding the skins was 6.5 and the final pH was 10.0.

Example 3

4650 pounds goat skins were placed in a bath consisting of 18,600 pounds water at 92° F. to which was added 23 pounds fused sodium sulphide (62% Na_2S approximately) and 72 pounds boric acid. Then there was added 23 pounds of a bacterial protease absorbed on wood flour. After being left overnight the skins are washed to remove sulphides. The pH before addition of the skins was 8.25; after the skins were in the bath one hour the pH was 9.0 and the final pH, before washing, was 9.3.

Example 4

2400 pounds goat skins (Brazils) were washed in water at 80° F. for 30 minutes. The skins were transferred to a paddle reel containing 675 gallons water at 86° F. to which had been added 12 pounds fused sodium sulphide (62% Na_2S approximately), 1 1/2 gallons muriatic acid (14° Bé.) and 4 pounds 14 ounces of an enzymatic pancreas preparation absorbed on wood flour. The pH of the bath before addition of the skins was 7.2. The skins were left 20 minutes and paddled 5 minutes. pH 10.9. Left for 25 minutes and paddled 5 minutes. pH 11.4. Left 30 minutes. There was then added 9 pounds ammonium sulphate. The skins were paddled 10 minutes and left overnight. pH at this stage 8.8. The liquor was then removed and the skins washed for 20 minutes with water at 86° F. Then there was added 9 pounds of a pancreas preparation of standardized enzymatic strength and 6 ounces ammonium sulphate. pH 9.3. The skins were paddled for 35 minutes and 6 pounds of a disinfectant solution added. The skins were then left overnight. Final pH 10.2.

Example 5

790 pounds kid skins were placed in a bath consisting of 380 gallons of water to which had been added 3.25 pounds ammonium sulphate, 1.6 pounds of a proteolytic enzyme of bacterial ori-

gin absorbed on wood flour and 8 pounds of ammonium sulphide solution (7% H_2S by titration). The pH before addition of the skins was 8.7. The skins were left overnight and washed.

Example 6

1600 pounds kid skins were washed for 20 minutes. The skins were then put in a bath consisting of 770 gallons of water at 90° F. to which had been added 8 pounds fused sodium sulphide (62% Na_2S approximately), 20½ pounds hydrochloric acid (12° Bé.), 4.8 pounds ammonium chloride and 3.25 pounds of a pancreas preparation of standardized enzymatic strength absorbed on wood flour. The skins were left for 20 minutes and washed. pH before washing was 8.3.

Example 7

1360 pounds kid skins were washed for 20 minutes. The skins were then put in a bath consisting of 650 gallons of water at 90° F. to which had been added 3.5 pounds ethyl mercaptan and 2.75 pounds of a pancreas preparation of standardized enzymatic strength absorbed on wood flour. The initial pH was 5.8. The skins were left for 20 minutes and washed.

Example 8

1390 pounds of kid skins were washed and put in a bath consisting of 670 gallons of water at 90° F. to which had been added 5.4 pounds thioglycolic acid neutralized with 3.5 pounds ammonia solution to a pH of 7.6 and 2.75 pounds of a pancreas preparation of standardized enzymatic strength absorbed on wood flour. The skins were left for 20 minutes and washed.

Example 9

2840 pounds of kid skins were washed for 30 minutes in wheels at 70–75° F. The skins were transferred to a paddle containing 1000 gallons water at 87° F., to which had been added 14 pounds fused sodium sulphide (62% Na_2S approximately) and 14 pounds muriatic acid (20° Bé.). The pH before addition of skins was 7.0; after addition 8.2; after 20 minutes 9.6. Then there was added 1.5 pounds of a pancreatic preparation of standardized enzymatic strength. After 5 minutes paddling 8 pounds ammonium sulphate was added, with paddling to mix. After 30 minutes pH was 9.0. The paddle was drained and refilled with water at 94° F. After 10 minutes washing, 9 pounds of a standardized bate preparation and 14 pounds ammonium sulphate were added. pH after 5 minutes paddling was 8.4. After 20 minutes paddling the skins were left for 2 hours with occasional paddling. pH 8.7. The paddle was drained and the skins washed 20 minutes with water at 85° F.

Example 10

678 pounds kid skins were washed in a drum for 15 minutes at 82° F. Then they were transferred to a paddle containing 235 gallons water at 92° F. H_2S gas was injected for 5 minutes with the paddle running. pH 9.4. Then there was added 5 pounds of an enzymatic bate preparation of standardized strength and the injection of H_2S gas with paddling continued for 15 minutes. pH 7.4. Approximately 2½ pounds H_2S were used up to this stage. The paddle was rested for 40 minutes. pH 7.9. H_2S was injected for 10 minutes with paddling, about 1.5 pounds being used. pH 7.4. Then there was added 1 pound of a dis-

infectant solution. The skins were left overnight. Final pH 8.1, temperature 87° F.

Example 11

2435 pounds kid skins were washed in a tumbler for 20 minutes at 82° F. The skins were then transferred to a paddle containing 6000 pounds water at 94° F. and paddled for 35 minutes. During this period CO_2 gas was injected and 16 pounds of an enzymatic bate and 9 pounds of a disinfectant were added. pH 8.3. The paddle was rested for 2 hours and then run for 30 minutes. At the start of this latter paddling, CO_2 gas injected to adjust the pH to its former value. During the last 5 minutes of this paddling, a mixture of 2 pounds sodium sulphide (32% Na_2S) and 6.25 pounds ammonium chloride, dissolved in some of the liquor, were added. pH then approximately 8.1. The paddle was rested overnight. pH 7.9. The skins were then paddled for 5 minutes, warmed up to 96° F. and paddled for 25 minutes. The sodium sulphide-ammonium chloride treatment of the previous day was repeated, using same quantities. pH then 8.2.

Example 12

370 pounds of kid skins were washed for 30 minutes and transferred to a paddle containing 1300 pounds of water at 96° F. to which had been added 1.8 pounds ammonium sulphate. After 5 minutes there was added 3¼ pounds of an enzymatic bate. 1.8 pounds of ammonium sulphate were then added, adjusting the pH to 8.5. The paddle was rested for 4 hours, after which 1½ ounces calcium sulphide were added. The paddle, after mixing, was rested overnight. pH then 8.7.

Example 13

1675 pounds kid skins were washed for ½ hour and transferred to a paddle containing 1600 pounds used old bate liquor taken from a previous fermented bate and 3400 pounds water at 96° F. There was then added a mixture of 20 pounds of an enzymatic bate preparation, comprising 0.8 pound of calcium sulphide with 5.8 pounds ammonium chloride and 6.6 pounds boric acid. The skins were paddled 20 minutes. pH 8.9. The paddle was rested overnight during which time the liquor was fermenting. The skins were removed and the paddle drained and refilled with water at 116° F. The skins were then put back and 7 pounds more of the same mixture were added. After paddling for 1 hour, there was added 4 pounds of a bate mixture like the first except for the absence of the calcium sulphide. The skins were then paddled for 2 hours.

Example 14

455 pounds skins were washed for 30 minutes and transferred to a paddle containing 1600 pounds water at 96° F. and 1.8 pounds of a mixture consisting of an enzymatic bate of pancreatic origin absorbed on wood flour, about 25%, calcium sulphide, about 5%, and ammonium chloride, about 70%. The paddle was run for 1 hour and rested 1 hour. pH 8.6. There was then added 1.8 pounds of the same mixture. After thorough paddling, the skins were rested overnight. Final pH 8.5.

What is claimed is:

1. A bating composition which comprises a mixture, in dry form, of a proteolytic enzymatic preparation, a relatively water-insoluble alkali-

alkaline earth sulphide and a neutralizing agent.

2. A bating composition which comprises a mixture, in dry form, of calcium sulphide, a neutralizing agent and a proteolytic enzymatic preparation absorbed on wood flour.

3. A bating composition which comprises a mixture, in dry form, of a proteolytic enzymatic preparation absorbed on wood flour, a relatively

water-insoluble alkali-alkaline earth sulphide and a neutralizing agent, the relative proportions by weight being sulphide 5 to 10%; neutralizing agent 60 to 80%; and proteolytic enzymatic preparation, including the wood flour, by balance.

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