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JOHN D. HASEMAN, OF LINTON, INDIANA

SOLID SILICIC ACID CONTAINING BLEACHING AGENTS AND PROCESS OF MAKING THE SAME

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This invention relates to bleaching agents and particularly to solid silicic acid containing bleaching agents of the general nature of fuller's earth and other silicon containing bleaching earths now used in removing color from animal, vegetable and mineral oils.

My invention is chiefly concerned with activated silica or more exactly, solid silicic acid or acids having unusual bleaching efficiency which may be transformed into inactive silica by removing the combined water contained therein, as by being heated to a very high temperature.

I have discovered that a solid silicic acid containing bleaching agent having very high bleaching efficiency and low oil retaining capacity can be readily and satisfactorily obtained from indianite, halloysite, bentonite and other clays or clay-like earths which upon the addition of a mineral acid such as sulfuric acid, yield a substantial amount of alum or other soluble aluminum salt or salts of the acid used, by treating such clays or clay-like earths with a mineral acid, preferably sulfuric acid, removing the resulting solution of aluminum salt or salts and heating the residue to remove the free water and a part but not all of the combined water therefrom.

I have discovered that my improved solid silicic acid containing bleaching agent can be obtained from alkali metal silicates such as water glass, by treatment with a mineral acid such as sulfuric acid, washing the solid product obtained and heating it to remove the free water and a part but not all of the combined water.

I also have discovered that silicic acid containing solid bleaching agents of the character now in use as well as the improved product produced in accordance with my invention are rendered materially more efficient in their bleaching action if used in association with and preferably in intimate mixture with alumina and by this term as used herein I mean to include both aluminum oxid and aluminum hydroxid as both may be used to serve the purpose stated.

I also have discovered that fuller's earth and other bleaching earths now in use for removing color from animal, vegetable and mineral oils can be materially improved with respect to their bleaching activity and at the same time so modified as to retain less of the oil treated therewith by diminishing the porosity of such solid bleaching materials as by wholly or in part sealing or stopping up their pores by depositing on the surface of such material and within their pores colloidal material preferably my silicic acid containing solid bleaching agent and more particularly such agent obtained from an alkali metal silicate as hereinbefore referred to and with which bleaching agent is preferably associated a relatively small amount of alumina.

In the practice of my invention based upon the discoveries referred to I treat indianite, halloysite, bentonite or other clays or clay-like earths which upon the addition of mineral acid, such as sulfuric acid, yield a substantial amount of a soluble aluminum salt or salts of such acid, with a mineral acid, preferably sulfuric acid, and remove the resulting solution of the soluble aluminum salt or salts produced. The residue is then washed substantially free from acid and other soluble impurities and heated to a temperature sufficient to drive off all of the free water and a part of the combined water.

In the preferred treatment of indianite, I mix approximately 925 pounds of commercial sulfuric acid of approximately 90 per cent. strength with 1,850 pounds of water and to the resulting diluted sulfuric acid I add 1,000 pounds of indianite, preferably ground to from 20 to 100 mesh. The mixture is heated to about its boiling point for from one-half to five hours preferably under ordinary conditions for about one hour and a half and the resulting solution of soluble aluminum salts consisting chiefly of alum separated from the residue by decantation, filtration or otherwise. The alum may be removed from the solution as by crystallization, separated from the impurities present as by recrystallization and marketed. The residue remaining after the separation of the solution of the soluble aluminum salt or salts is then washed with water until substantially

acid free and heated to remove the free water and part of the combined water present therein. In practice I slowly raise the temperature of the residue to a dull red heat, such heat serving to drive off all of the free water present and a part but not all of the combined water. I prefer to remove about half of the combined water. The material is then allowed to cool and ground to a degree of fineness depending upon the character of the bleaching process in which the material is to be used. If the material is to be employed for bleaching by the filtration method, which is commonly used in bleaching animal and vegetable oils, I prefer to grind the material to about 200 mesh. If the material is to be employed for bleaching by the percolation method, which is commonly used in the bleaching of mineral oils, the material is preferably ground to from 20 to 60 mesh. It may be produced in much coarser form if desired.

In the preferred practice of preparing my bleaching agent from halloysite I first mix 1,400 pounds of sulfuric acid with 2,800 pounds of water and to this I add 1,000 pounds of halloysite preferably ground to from 20 to 60 mesh. The mixture is allowed to boil slowly for preferably about one hour and a half and the resulting solution of soluble aluminum salts consisting principally of alum removed by decantation or otherwise. The alum may be separated, purified and sold. The residue is then washed substantially acid free and slowly heated to a dull red heat as described above.

In the preferred treatment of bentonite I preferably mix 400 pounds of commercial sulfuric acid with 800 pounds of water and to this I add 1,000 pounds of bentonite preferably ground to 20 to 100 mesh. I then boil the material for preferably about one hour and a half. The resulting solution which contains aluminum sulfate, iron sulfate and other soluble salts, is removed by decantation or otherwise and the residue washed and heated to a dull red heat as set forth above. In each case I prefer to drive off only about one-half of the combined water present.

Indianite, halloysite, bentonite and other clays or clay-like earths of the character hereinbefore referred to ordinarily contain some aluminum in the form of oxid or hydroxid, generally the latter, and in treating these materials I preferably add in each case an insufficient quantity of the sulfuric acid to transform all of the aluminum oxid or hydroxid present into aluminum sulfate. I preferably employ the sulfuric acid in such proportion with respect to the material under treatment that there remains in the residue from 2 to 10 per cent. of the aluminum oxid or hydroxid. My product ordinarily contains about 5 per cent. of alumina but it may contain a much smaller or larger proportion of alumina. I may produce a satisfactory bleaching agent by the use of such an amount of the mineral acid as to dissolve and remove all of the aluminum oxid or hydroxid present but the product thus produced, being free from alumina, is not as efficient a bleaching agent as the product is when it contains a relatively small proportion of the aluminum oxid or hydroxid. The presence of the alumina materially improves the bleaching efficiency of the product.

I can satisfactorily produce my solid silicic acid containing bleaching agent by mixing commercial water glass of the strength commonly used in egg preservation, of specific gravity approximately 1.7, with aluminum hydroxid in the preferred proportion of 1,000 pounds of sodium silicate to 150 pounds of soluble aluminum hydroxid and adding thereto preferably 800 pounds of dilute sulfuric acid produced by mixing 320 pounds of commercial sulfuric acid with 480 pounds of water. The mixture is boiled for about one hour and a half and the solution of aluminum and sodium salts removed by decantation or otherwise. The residue is then washed substantially acid free and slowly heated to a dull red heat to drive off the free water and a part of the combined water as hereinbefore explained. The resulting solid product is then ground to the desired degree of fineness depending upon the bleaching process in which the material is to be used.

In place of using sodium silicate as described above I may produce my improved bleaching agent by treating 1,000 pounds of high grade kaolin such, for example, as the American Kaolin Company's Georgia kaolin, with 500 pounds of commercial sodium hydroxid of about 96 per cent. strength dissolved in 3,300 pounds of water. This mixture is boiled for preferably one and one-half hours. To the resulting product I add 1,500 pounds of commercial sulfuric acid and boil for about one and one-half hours. The resulting solid product is then separated from the solution by decantation, filtration or the like and thoroughly washed with water until it is substantially acid free. It is dried by slowly heating to a dull red heat, care being taken not to heat the material above this point. The dry product is finely ground to a degree of fineness depending upon the bleaching process for which it is to be used as explained above.

The bleaching material produced by my process as above set forth is a silicic acid containing solid bleaching agent bearing it is thought substantially the same relation to silica which activated carbon bears to ordinary carbon. It is with absolute conviction believed to be solid silicic acid or a mixture of silicic acids.

In the practice of my process care must be

taken to prevent the bleaching properties of my material being destroyed by heating the material above the temperature at which such action takes place. If the material is heated to materially above a red heat its bleaching power is to a certain extent destroyed and if heated to a white heat its bleaching power is entirely destroyed. This is believed to be due to decomposition of the silicic acid or acids at the high temperatures referred to. The removal of all of the water of constitution from the material reduces it to silica and destroys its bleaching capacity.

Theoretically there are monosilicic acid, disilicic acid and trisilicic acid as the salts of such acids are known. I have been unable to determine whether or not the silicic acid which I produce is the monosilicic acid, disilicic acid or the trisilicic acid, but it is believed that all of these silicic acids are produced in my process with the disilicic acid forming by far the greater proportion of the mixture of such acids, although it may be that only the disilicic acid is produced.

The bleaching power of fuller's earth or other silicon containing bleaching agent is substantially in proportion to its relative acidity. My composition produced as above described has a relative acidity which is more than twice that of the best fuller's earth now in use, as, for example, what is known in the trade as Floridian XXF fuller's earth. Its bleaching power is more than double that of Floridian XXF fuller's earth. The material also differs greatly from fuller's earth and other bleaching earths with respect to porosity. Its pores are finer and of materially less volume than the pores of fuller's earth, its absorbing capacity for oil being at least 50 per cent. less than that of fuller's earth. In consequence of its lesser degree of porosity it retains at least 50 per cent. less of the oil bleached therewith. Its use therefore has the advantage that a given quantity of it will bleach to standard color two or three times as much oil as can be so bleached by a corresponding weight of fuller's earth and the retention of oil as indicated above is at least 50 per cent. less, whereby an important economy in the bleaching of oil is obtained.

I have found that my improved silicic acid containing bleaching material can be deposited upon and to some extent within the pores of fuller's earth and other similar silicon containing bleaching earths thereby increasing the bleaching activity of such bleaching earth and lessening its retention of oil bleached therewith. In the preferred practice of this modification of my invention I add to 1,000 pounds of commercial fuller's earth approximately 1,000 pounds of commercial sodium silicate (water glass) of the strength commonly used in egg preservation and about 500 pounds of water to which may advantageously be added about 100 pounds of aluminum hydroxid. The materials are then thoroughly mixed and boiled for about one hour. To this mixture I then add 500 pounds of commercial sulfuric acid and boil for about one hour and a half. The first boiling operation can be omitted, but I have found in practice that such boiling is an efficient way of depositing my material upon the surface of and within the pores of the fuller's earth. The second boiling operation is, however, necessary in order to produce my silicic acid containing bleaching agent upon and within the bleaching earth. The fuller's earth or the like treated as above described is allowed to cool and is thoroughly washed and dried. The drying operation is performed in the manner above described by slowly heating to a dull red heat to remove the free water and a part of the combined water, care being taken to avoid heating to materially above a dull red heat. The resulting material will, even if the alumina is omitted, bleach to standard color materially more oil than the original fuller's earth and will retain materially less of the oil than the untreated fuller's earth. If the alumina is added, as is preferred, the bleaching efficiency of the product is still further enhanced.

The product produced in the manner last described has not as great oil bleaching efficiency as my activated silica or silicic acid or acids employed alone but is superior in bleaching efficiency to the best fuller's earth obtainable and is adapted for economical commercial use.

I may with some degree of practical success wholly or partially seal or stop up the pores of fuller's earth or like bleaching earths otherwise than in the manner described. I have found that the pores of such earths may to a considerable extent be sealed by thoroughly mixing with 1,000 pounds of such earth, preferably high grade fuller's earth, a mixture or suspension of 30 pounds of kaolin, preferably of the grade known in the trade as American Kaolin Company's Georgia kaolin, in 5,000 pounds of water. The kaolin suspended in the water is to a considerable extent absorbed in the fuller's earth and the pores thereof are sealed or stopped up to a considerable extent. The thus treated fuller's earth is heated to evaporate the water present and preferably slowly heated to a dull red heat to drive off the free water and a part but not all of the combined water. The product thus obtained has increased bleaching efficiency as compared with the original fuller's earth and retains less of the oil bleached therewith.

While I have described in detail the various embodiments of my invention and the preferred processes employed in producing the same it is to be understood that my invention is not restricted to the proportions

of ingredients, details of procedure, and the like except as set forth in the appended claims.

This application is in part a continuation of my copending application Serial No. 713,630, filed May 15th, 1924, for fuller's earths and certain other clays and siliceous materials, as to the common subject matter set forth in the five paragraphs immediately preceding.

My composition while primarily intended for bleaching purposes has been found to be particularly well adapted for use in absorbing or taking up gasoline and other volatile hydrocarbons from natural gas. When intended for such use the composition need not be finely ground but may advantageously be in the form of coarse granules or it may be formed into small cubes, or other shapes. In making this use of my composition the gas is passed through the material until a considerable quantity of the volatile hydrocarbons have been taken up. The material is then heated to about 200° C. or above to drive off hydrocarbons thus taken up and the vapors condensed. The composition after the removal of the hydrocarbons is ready for reuse.

I claim:

1. The herein described process comprising reacting upon silicic acid containing clay-like earths normally containing aluminum oxid or hydroxid and which upon treatment with sulfuric acid yield a substantial amount of aluminum sulfate, with a dilute mineral acid in such amount as to dissolve a part but not all of the aluminum oxid or hydroxid present, removing the resulting aluminum salt solution, washing the residue and heating it to a temperature sufficient to remove a part but not all of the combined water present therein.

2. The herein described process comprising reacting upon silicic acid containing clay-like earths normally containing aluminum oxid or hydroxid and which upon treatment with sulfuric acid yield a substantial amount of aluminum sulfate, with dilute sulfuric acid in such amount as to dissolve a part but not all of the aluminum oxid or hydroxid present, removing the resulting aluminum salt solution, washing the residue, heating it to a temperature sufficient to remove a part but not all of the combined water present therein and grinding the product to powdered form.

3. The herein described process comprising mixing dilute sulfuric acid and powdered indianite in the approximate proportions of 810 parts by weight of sulfuric acid, 1,940 parts by weight of water and 1,000 parts by weight of indianite, boiling the solution, separating the resulting solution of alum and other salts, washing the residue until substantially free from acid, heating the residue to a dull red heat, and grinding the product.

4. A bleaching material comprising a porous oil-bleaching argillaceous material having its porosity diminished by the presence of a deposit comprising an intimate mixture of alumina and a solid silicic acid-containing compound which normally contains water of constitution but containing less than its normal content of such water.

5. A bleaching material comprising a fuller's earth having its pores diminished by the presence of a deposit comprising an intimate association of alumina and a solid silicic acid-containing compound which normally contains water of constitution but containing less than its normal content of such water.

6. The herein described process which comprises subjecting a silicic acid-containing compound which normally contains water of constitution and is reducible to inert silica upon being heated to a white heat, to a sufficient temperature to remove a part but not all of its combined water, and reducing the thus treated silicic acid-containing compound in admixture with alumina to a finely divided condition.

7. The herein described process comprising subjecting a silicic acid-containing compound normally containing water of constitution and reducible to inert silica upon being heated to a white heat, to a sufficient temperature to remove a part but not all of its combined water, mixing alumina with the resulting product, and grinding the mixture to finely divided condition.

In testimony whereof I affix my signature.

JOHN D. HASEMAN.