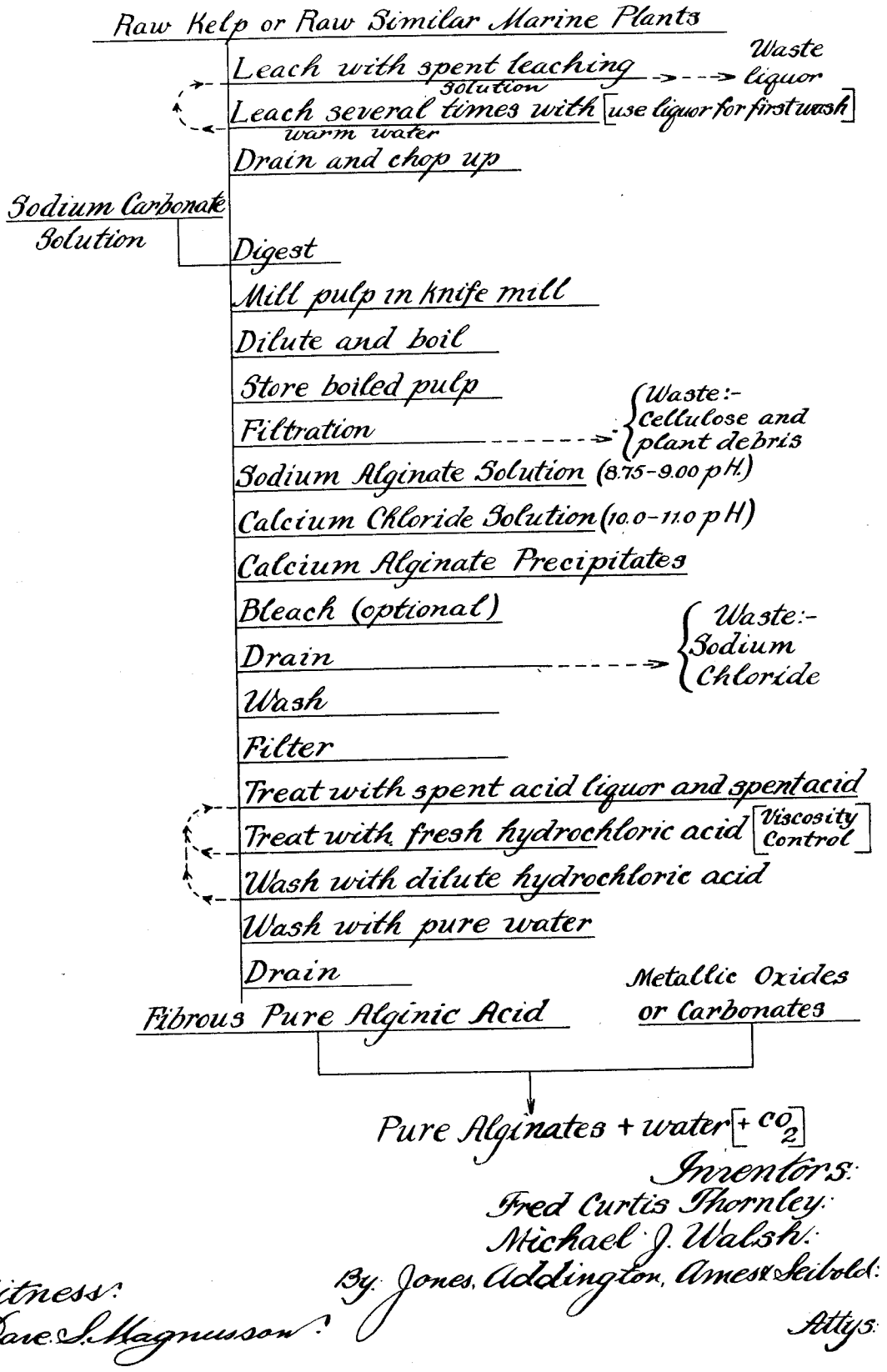
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PROCESS OF PREPARING ALGINIC ACID AND COMPOUNDS THEREOF

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PROCESS OF PREPARING ALGINIC ACID AND COMPOUNDS THEREOF

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The present invention relates to an improved process for the manufacture of free alginic acid and of alginates in a state of purity, and in a form not hitherto made.

One of the objects of our present invention is to prepare fibrous free alginic acid in a form in which it may readily be filtered and otherwise treated for the removal of objectionable salts, acids and metallic radicals therefrom.

A further object of our present invention is to prepare alginates, and especially metallic alginates that are substantially free from acid radicals other than that of alginic acid, and which do not contain more than mere traces of an excess of metallic radical over that required for the exact neutralization of the alginic acid.

The industrial application of both soluble and insoluble alginates, and of alginic acid has been hindered in the past by reason of the fact that the alginates and alginic acid prepared by known methods were so impure and contaminated with either excess alkali, or with undesirable salts, that they would not act uniformly and dependably, and that the user of such alginates or alginic acid was compelled to experiment and modify his process in which he employed the aforesaid substances with each batch of alginic acid or alginate that he purchased.

It is one of the objects of our invention to prepare metallic and other alginates, and free alginic acid, in an exceptional state of purity, and to do so by methods that lend themselves to practical large scale production under conditions which render the process commercially applicable.

Another object of our present invention is to prepare free alginic acid in fibrous form, in which form it lends itself exceptionally well to washing and purification, and also to filtration by mechanical equipment.

Still another object of our invention is to prepare a metallic alginate, for example calcium alginate, by the precipitation of an alkali alginate by a solution of a metallic salt, such as a calcium salt, and to carry out said precipitation under controlled conditions as regards the hydrogen ion concentration of the solutions involved in the precipitating reaction, so that the metallic alginate, such as calcium alginate, may be precipitated in a fibrous form, in which it lends itself most readily to filtration washing and purification.

Other objects of our invention will appear in connection with the description and drawing which accompany the present application and form a part thereof.

The raw material employed for carrying out our improved process comprises marine plants or algæ that contain alginic acid compounds. Such plants are sea-weeds and are found in large amounts at or near the coast, especially that of the North Pacific or North Atlantic Ocean. Among the types which have proven to be particularly advantageous are the marine plants that belong to the general class Phaeophyceae, the so-called Laminariae such as Laminaria digitata, Laminaria saccharina, Laminaria cloustoni, and especially the giant kelps of the Pacific such as Macrocystis and Nereocystis, the latter two being very abundant along the shore of the Pacific Ocean in California.

For the sake of simplicity we will hereinafter refer to all of these plants by the common name of "kelp", by which we intend to cover any or all, or mixtures, of the above marine plants or algæ, such as may be harvested along and near the shores of the oceans, and irrespective of the particular species involved, as we have found that all marine plants that contain sufficient amounts of alginic acid compounds may be used for carrying out our herein described process of preparing alginic acid.

The average alginic acid content of the marine algæ that we prefer to employ in our present process is about 4 percent of the weight of the leached freshly harvested kelp.

According to one exemplification of our method for preparing substantially pure fibrous alginic acid in accordance with our present invention we proceed substantially in the following manner, although it is to be understood that the method about to be described is purely illustrative, and that obvious modifications within the skill of the

chemist may be made therein, without departing from the spirit of our present invention.

The raw kelp, which grows in abundance near the seashore, is harvested, preferably by under-water cutting and is brought to the converting plant in a harvesting boat. This kelp consists preferably of macrocystis, which is a common giant kelp indigenous to California coastal waters.

The raw kelp is transferred from the harvesting boat to pre-leaching tanks in which the kelp is subjected to a leaching with leach liquors derived from further leaching operations that are about to be described. This preliminary leaching is done at ordinary temperatures, and has for its object the removal of most of the adherent salts and absorbed salt solutions derived from the sea water in which the kelp grew.

After the pre-leaching step, the kelp is transferred to the leaching tanks in which it is treated with two successive treatments with warm water, having a temperature approximating 140° F. The leach liquors derived from this treatment of the kelp are those that are employed for the pre-leaching step described above.

The kelp is then drained as free as possible from the leaching liquors, is roughly chopped up, and then transferred to digesting tanks wherein it is treated with a solution containing an amount of sodium carbonate (Na_2CO_3) approximately equivalent to 4% of the weight of the leached and chopped kelp.

The amount of sodium carbonate necessary is calculated by estimating the weight of the kelp from its volume, a definite factor of a given number of pounds per cubic foot being used and which factor is readily calculated from a few tests on a particular type of kelp undergoing treatment. The treatment of the chopped kelp with the sodium carbonate solution lasts for about an hour, the mixture of kelp and solution being heated by the admission of live steam. Enough water is used with the chopped kelp and sodium carbonate to form a heavy pulp. The heating of the mixture by the steam disintegrates the kelp further, and the resultant mass has the consistency of a rough pulp.

The next step consists in grinding the rough pulp obtained as a result of the digesting treatment above described in a comminuting machine having rotating knives, such as for example a machine known as a "Williams mill", which will convert the pulp into a much more finely divided state, so that the sodium carbonate will act more completely upon the alginic compounds contained in the kelp undergoing treatment.

The pulp issuing from the said comminuting machine or mill is next distributed among three tanks, in which it is diluted at about 140° F. with five times its volume of warm water. The diluted pulp thus obtained is boiled by the injection of live steam for a period of from one to one and a half hours, whereupon the creamy pulp formed as a result of the boiling is pumped to storage tanks.

The next step comprises passing the diluted pulp through a filtering system to remove the cellular débris of the kelp and any other undissolved matter. This filtration may take place in common bag filters, but it is preferred to carry out this step in mechanical rotary suction filters of the type known as "Oliver" filters. In order to speed up the filtration and to keep the filtering surface from clogging, and to obtain a more easily washed filter cake, the dilute pulp that is to be filtered receives the addition of a small amount of a filter-aid, such as a diatomaceous earth, preferably of the type known as "filter cell", and particularly of the grade known as "Hy-Flo". The filtrate obtained as the result of this operation is a solution of sodium alginate.

The next step in the process of preparing fibrous alginic acid in accordance with our present invention comprises the formation of a special fibrous form of an insoluble alginate. For the purpose of illustration only, and without limiting ourselves in any way to the use of calcium salts, we will now describe the operations as they are performed when calcium salts are used. Of course, it is also to be understood that alkalies other than sodium carbonate may be employed in the first part of the digestion step as already described, and that we have chosen sodium carbonate simply as an illustrative example, as obvious substitutes for the sodium carbonate may be used with equal effect. Such substances are potassium carbonate or other sufficiently alkaline-reacting salts may be employed as substitutes for the sodium carbonate.

Supposing, for the purpose of illustrating our process, that calcium alginate is the insoluble alginate that is to be prepared, we may proceed substantially as follows:

A solution of calcium chloride having a hydrogen ion concentration of from pH 11.5 to pH 10.0 is prepared and placed in a precipitating tank provided with an efficient rapid mixing and agitating device, such as a number of propellers, usually two, running at the rate of 1800 R. P. M. This type of agitator known as "lightning" agitators has been found satisfactory. The dilute solution of the alkaline alginate, as for example the sodium alginate made as above described, and which has been tested for its hydrogen ion concentration which is adjusted so that it will not fall below pH 7.5 at any time, is run into the calcium chloride solution while the latter is violently and constantly agitated

throughout the addition of the sodium alginate solution. This manner of procedure is important, as by exercising control over the hydrogen ion concentration and the method of mixing, namely by adding the sodium alginate solution to the calcium chloride solution (and not in the opposite sense) we obtain very pronouncedly beneficial results. These results are the precipitation of insoluble calcium alginate in the form of fibers which have much the appearance of cotton fibers, but are grayish green in color.

These fibers differ from the calcium alginate obtained when calcium chloride and sodium alginate are brought together indifferently, as in that case the calcium alginate will be precipitated in a gelatinous gummy form that is practically impossible to filter, and still more difficult to wash free from excess reagents. Our present process, by providing a means of obtaining the calcium alginate in the fibrous, non-gelatinous filterable form sharply differentiates our process from the known methods of preparing calcium alginate.

After all the sodium alginate solution has been added to the calcium chloride solution as above set forth, the agitation is continued for a further period of ten minutes to ensure the entire completion of the reaction between the calcium chloride and the sodium alginate. The reaction that takes place may be exemplified by the following equation. In this equation we express the alginate radical by an arbitrary designation "Alg", and as alginic acid appears to have a number of replaceable hydrogen atoms we have designated this condition by writing the empirical formula for alginic acid $Alg(H)_n$. The reaction takes places quantitatively:

(1) $Alg(Na)_n + \times CaCl_2 = Alg(Ca)_{n/2} + 2 \times NaCl.$

It will thus be seen that one of the products of the reaction is sodium chloride, which is soluble, and the other is the insoluble fibrous calcium alginate. The admixed solution of calcium chloride and sodium alginate, which by the metathesis as set forth in the above reaction (1) now comprise the insoluble fibrous calcium alginate and a solution of sodium chloride, is now allowed to rest until the calcium alginate separates out. By reason of its specific gravity and the density of the solution, the said calcium alginate will rise to the surface and form a fibrous matted layer under which the solution of sodium chloride rests.

The sur-natant solution is thereupon drawn off, and the precipitated calcium alginate is sludged up with water until it forms a pulp suitable for filtration on such mechanical filters as the already-mentioned "Oliver" filters. The calcium alginate, which forms a fibrous mat on the filtering surface, is washed with water, and finally comes off the Oliver filter as a fibrous cake containing from 15 to 20% of solids.

If it be desired to remove the aforesaid grayish-greenish color from the calcium alginate and to produce a substantially colorless alginic acid, then the calcium alginate may be bleached by treatment with an appropriate bleaching agent.

We have found it advantageous to carry out the bleaching step at the stage where the calcium alginate has first been precipitated, and to employ for this purpose a solution of sodium hypochlorite. This we accomplish substantially as follows, although we do not wish to be limited to this particular method of bleaching, as other bleaching agents than hypochlorite may be used, and the following example is merely illustrative.

After the sur-natant solution has been drawn off from the precipitated calcium alginate and the precipitated calcium alginate has been sludged up with water until it forms a pulp, a predetermined quantity of bleaching solution is added in order to bleach the calcium alginate. The quantity of bleach solution, which may be sodium hypochlorite solution of commerce or other soluble alkali hypochlorite, varies from one gallon to one and one half gallons per 500 gallons of pulp, according to the degree of bleaching desired. The bleached calcium alginate is then ready for filtering in the same manner as it would be if no bleaching had taken place.

Obviously, other insoluble alginates than those of calcium can thus be bleached.

While it is possible to bleach alginic acid otherwise in its manufacture, we have found that the bleaching is most effective, most controllable and least injurious to the ultimate alginic acid and salts when carried out at this point in the process.

In this form the calcium alginate is ready for commerce, or, also in accordance with our present invention, may be at once converted into substantially pure fibrous alginic acid. This we accomplish substantially as follows.

In order to convert the calcium alginate into free fibrous alginic acid, which is also insoluble in water, we make use of the following reaction:

(2) $\times Alg(Ca)_n + yHCl = \times Alg(H)_{2n} + CaCl_2$

Accordingly, we treat the fibrous calcium alginate, while in suspension in water, with a solution comprising hydrochloric acid, which brings about the above reaction (2). We have found that it is much more advantageous to carry out this reaction in a number of stages or steps, and for this reason first treat the insoluble fibrous calcium alginate with the acid liquors derived from a previous treatment of a batch of calcium alginate with hydrochloric acid. As reaction (2) is re-

versible to some extent, a much more complete conversion of the calcium alginate into free alginic acid is realized when working in this manner. During the entire treatment with the acid liquors from a previous batch the calcium alginate and acid liquor is kept in a violent state of agitation by means of mixers like the aforesaid "Lightning" mixers, so as to insure intimate and uniform contact of the acid with the alginate. The first treatment is kept up for about one half hour, with constant agitation, whereupon the fibrous free alginic acid, which at this stage however still contains some calcium by reason of the partial reversibility of the reaction (2) is screened off from the liquor in which it is suspended, so as to remove the calcium chloride that has been formed by the combination of the hydrochloric acid in the treating liquor with the calcium of the insoluble calcium alginate.

The partially purified alginic acid collecting on the screen, and which screen may be of the rotary suction-filtering type, is transferred back to the treating tank and is then treated with a solution of hydrochloric acid, in about the proportion of 16 gallons of 30% hydrochloric acid to a total volume of 400 gallons. This fresh solution of hydrochloric acid will complete the conversion of the calcium alginate into free alginic acid as there will now be but little calcium chloride in the solution, so that the reverse of the reaction (2) can not take place to any appreciable extent.

The second treatment of the calcium alginate or rather the now partially pure alginic acid is for thirty minutes, with constant agitation. The alginic acid is then filtered off by employing a rotary screen as already described. The liquor separated from the alginic acid is employed for the first treatment of the subsequent batch of calcium alginate as stated above. The sequence of the operations and the return of the liquors, such as leach liquors, acid liquors etc. into the system is plainly shown on the diagrammatic drawing showing a flow-sheet of the process, and which drawing forms a part of the present specification.

After the free fibrous alginic acid has been screened from the liquor containing the excess hydrochloric acid, it is again transferred to the treating tank and is washed therein by being mixed with very dilute hydrochloric acid, the solution however always being kept sufficiently acid to maintain an hydrogen ion concentration of from pH 2.25 to pH 3.0. Care is also taken to accomplish this washing with soft water, that is to say with water that is substantially free from calcium and magnesium salts. We have found water that has been treated by zeolites, such as "permutite" to be suitable, the fibrous alginic acid being agitated in the water for 30 minutes, and then again passed over the screen to remove the acid wash-water.

The alginic acid is then transferred back to the treating tank for a third time, and once more subjected to agitation and washing with slightly acidulated "soft" water free from calcium and magnesium salts. It is finally passed over rotary filters of the continuous type, such as "Oliver" filters. The fibrous mat of alginic acid coming from these Oliver filters is again mixed with water to form a pulp, enough acid having been added to the water to maintain its hydrogen ion concentration at substantially from pH 2.25 to pH 3.0, and the alginic acid is then again filtered on a second Oliver filter, the filter cake forming in the final filtration being washed with soft water to remove any hydrochloric acid that might remain. The final filter cake is in the form of a fibrous mat containing from 12 to 15% of solids.

The alginic acid as made by the above process is in the form of fibers and is a novel product; and we are not aware that free alginic acid, substantially free from foreign acids and metallic radicals, has ever been prepared prior to our herein disclosed process.

Other methods purporting to produce free alginic acid invariably refer to the same as a gelatinous, slimy mass, and one that can be filtered only with extreme difficulty, if at all. By carefully controlling the conditions of precipitation of the calcium alginate, and by also carefully controlling the treatment of the said calcium alginate so as at no time to destroy its fibrous nature, we have succeeded, by our present process, in preparing substantially pure fibrous alginic acid.

Our researches have shown that alginic acid has a large number, at least seven, active hydroxyl groups, the hydrogen atoms of which groups are replaceable by metals or by organic radicals, and in consequence thereof it becomes possible to prepare alginate salts having acid characteristics, as well as salts that are completely saturated with substituting groups. Alginic acid, such as prepared by our present process, will readily combine with alkalies and bases to form soluble alginates, and will likewise combine directly with metallic oxides or hydroxides to form the corresponding insoluble or soluble alginates, as the case may be.

As already said, one of the objects of our present invention is the production of pure alginates, and to accomplish this purpose we proceed from the pure alginic acid made as above set forth.

In order to prepare an alginate free from other salts or acids, we preferably employ the oxide or carbonate of the metal whose alginate is to be prepared, so that the only other products of the reaction will be water,

or water and carbon dioxide. The reactions involved are as follows, the symbol $Alg(H)_n$ being used for alginic acid, as the molecular weight of this substance is so great that its precise chemical formula has not as yet been ascertained with any degree of certainty.

In the making of the alginate of a divalent metal for example, the following reaction, in which M'' stands for the divalent metal, may take place:—

$$(3).\ Alg(H)_n + \times M''O = Alg(M)_{n/2} + \frac{n}{2}H_2O$$

If the carbonate of the metal is used, the reaction might be written:

$$(4)\ Alg(H)_n + \times M''CO_3 = Alg(M)_{n/2} + \times CO_2 + n/2H_2O$$

As will be noticed, in either reaction (3) and (4) there are no other by products than water, or water and carbon dioxide. By basing our process on these reactions we are able to prepare definite and substantially pure alginates, which are free from impurities. For example the aliginates described in the literature are all made by the precipitation of an alkali alginate with the soluble salt of the metal whose insoluble alginate it was desired to produce. Obviously, the other product of the metathesis would have to be removed, but as many of the insoluble alginates are highly colloidal in nature, and tenaceously adsorb the other reaction products, it has not been found possible to prepare even approximately pure alginates free from metallic radicals or acid radicals other than alginic acid radicals by such precipitation methods. Our present method, on the contrary, allows of the preparation of pure alginates.

In determining the neutralization value of our free fibrous alginic acid we employ a method of electrometric titration, using sodium carbonate as the titrating solution. From the combining value thus obtained, it becomes possible to determine, merely by calculation, as is well understood in stoichiometry, the amount of other substances capable of combining with the alginic acid, as for example to calculate the amount of copper carbonate required to form copper alginate.

The preparation of magnesium alginate, for example, which is a water soluble substance, may be carried out, in accordance with our invention, substantially as follows: A quantity of fibrous alginic acid prepared as herein described is treated with an equivalent quantity of magnesium carbonate. The alginic acid is a sufficiently strong acid, despite its insolubility, to decompose the magnesium carbonate with the formation of soluble magnesium carbonate, water and carbon dioxide.

If copper oxide or copper carbonate be used, an exact amount of the said oxide or carbonate should be employed, as copper alginate is insoluble in water.

The preparation of other insoluble alginates, such as zinc alginate, nickel alginate, barium alginate and the like is carried out as described in connection with copper alginate.

Another object of our invention is the production of pure water-soluble double alginates of heavy metals or alkaline earth metals with ammonia. A particularly valuable and interesting double alginate is that of copper and ammonia. This can be prepared in pure form in accordance with our present invention, by treating substantially pure fibrous alginic acid with a calculated equivalent of pulverized copper oxide or carbonate in an incorporating machine in which the alginic acid and copper carbonate is actively agitated for about an hour until combination has taken place with the formation of the insoluble copper alginate. The equivalent amount of ammonium hydroxide is next added and the mixture agitated for about an hour, by which time the insoluble copper alginate will have reacted with the ammonium hydroxide to form the soluble cuprammonium alginate.

The process of making zinc-ammonium alginate is similar in every way to that of making cuprammonium alginate, as described above.

The alginates of the alkali metals can likewise be prepared free from other salts by adding to a known amount of free fibrous alginic acid, as prepared by our herein described method, a calculated equivalent quantity of an alkali carbonate or bicarbonate.

The alginates prepared in accordance with our present process are of a state of purity not hitherto attained, in commercial practice.

A still further object of our invention is the control of the viscosity of the soluble alginates. This control we accomplish by storing the kelp before the preliminary treatment or during the purification of the insoluble alginate.

We have discovered that the viscosity of the alkali alginates, such as sodium alginate, is proportional to the freshness of the kelp from which the solutions are prepared; in other words, the more the kelp is aged before treatment, the lower will be the resultant viscosity of the sodium alginate and other soluble alginates or double alginates prepared.

An alternative method for lowering the viscosity of the soluble alginates is to perform the acid treatment of the calcium alginate at a temperature of about 40° C. In this case the viscosity is inversely proportional to the time of treatment, in other words the longer the treatment, the lower the viscosity; or the more acid the solution,

the lower the viscosity; and finally the higher the temperature of treatment, the lower the viscosity. We believe, but do not wish to be bound by the said theory, that the lowering of the viscosity is caused by a partial depolymerization of the alginic acid molecule. In the case of aging the kelp this would result from fermentation; and in case of said treatment, by a species of hydrolysis or hydrolytic decomposition.

We wish it to be understood that the examples given in our present application are merely for purposes of illustration, as obvious modifications, such as would occur to a skilled chemist, may be made in our processes without departing from the spirit and scope of our invention, which we desire to be interpreted and limited only by the hereunto appended claims as viewed in the light of the prior art.

We claim as our invention:—

1. As a new article of manufacture, fibrous alginic acid.

2. As a new article of manufacture, fibrous partially dried alginic acid substantially free from metallic radicals and mineral acids.

3. As a new article of manufacture, alginic acid free from metallic radicals and mineral acids, in fibrous form.

4. As a new article of manufacture, fibrous partially dried alginic acid substantially free from metallic radicals and mineral acids.

5. As a new article of manufacture, alginic acid in fibrous form, and substantially free from mineral impurities.

6. The process of preparing pure fibrous alginic acid which comprises converting a soluble alginate into an insoluble alginate by adding such alginate to an agitated substantially non-acid solution containing a salt of a metal which will form with alginic acid an insoluble alginate, washing said insoluble alginate free from impurities, and treating the thus obtained insoluble alginate with an acid capable of forming a soluble salt with the mineral constituent of the insoluble alginate.

7. The process of preparing pure fibrous alginic acid which comprises converting a soluble alginate into an insoluble alginate in a substantially non-acid solution, washing said insoluble alginate thus produced, treating said insoluble alginate with an acid capable of forming a water-soluble compound with the metallic radical combined with the alginic acid radical, and washing the thus obtained alginic acid with water containing a small amount of acid.

8. The process of preparing pure fibrous alginic acid which comprises treating a soluble alginate with a solution of a metallic salt capable of forming insoluble alginates to precipitate an insoluble alginate in fibrous form, washing said insoluble alginate with water to remove excess uncombined metallic salt, treating the thus obtained insoluble metallic alginate with an acid capable of forming a soluble salt with the metallic radical that is combined with the alginic acid to liberate fibrous alginic acid, washing the thus formed free fibrous alginic acid with a solution kept slightly acid, and finally washing the purified alginic acid with water.

9. The process of preparing pure fibrous alginic acid which comprises treating sodium alginate with a solution of a salt capable of forming insoluble alginates to precipitate an insoluble alginate, filtering said alginate and washing the same, treating the thus obtained insoluble alginate with an acid to combine with the metallic radical that is in combination with the alginic acid so as to liberate fibrous alginic acid, filtering said fibrous alginic acid from the liquor and washing the same free from metallic radicals by means of water containing small amounts of acid, and finally washing the thus purified fibrous alginic acid with pure water.

10. The process of preparing pure fibrous alginic acid which comprises treating sodium alginate with calcium chloride to form insoluble calcium alginate in fibrous form, filtering off said fibrous insoluble calcium alginate, washing the same free from excess metallic salts, treating said fibrous alginate of calcium with a solution of an acid to liberate free fibrous alginic acid and form a water-soluble calcium salt, filtering off the liberated fibrous alginic acid and washing the same with acidulated water until it is substantially free from calcium salts, and finally washing the thus purified fibrous alginic acid with pure water.

11. The process of preparing pure fibrous alginic acid substantially free from metallic radicals, which comprises precipitating calcium alginate from solutions of calcium chloride and sodium alginate in a solution which is not acid at any time during said precipitaton, filtering off and washing the thus precipitated fibrous calcium alginate, treating the said calcium alginate with hydrochloric acid to liberate free alginic acid and form calcium chloride, filtering off the liberated alginic acid, washing the same substantially free from calcium salts with a solution of hydrochloric acid, and finally washing the purified alginic acid with pure water.

12. The process of preparing pure fibrous alginic acid substantially free from metallic radicals, which comprises treating a fibrous insoluble alginate with an acid capable of forming a soluble salt with the metallic radical contained in said insoluble fibrous alginate, washing the thus formed fibrous alginic acid with a slightly acid solution to remove substantially all the metallic radicals therefrom, and washing the thus obtained and purified alginic acid with pure water.

13. The process of preparing pure fibrous alginic acid from marine plants containing alginates which comprises leaching said marine plants with water to remove adherent and adsorbed salts inherent therein, comminuting the said plants and treating the same with alkalies to form a solution of an alkali alginate, filtering the cellular débris and insoluble matter from the said solution, precipitating an insoluble alginate from the said solution by an admixture with a metallic salt forming an insoluble alginate, carrying out said precipitation in a medium having an hydrogen ion concentration not below substantially pH 7.0, separating and washing the precipitated insoluble alginate, liberating free fibrous alginic acid from said insoluble alginate, washing the liberated fibrous alginic acid with water containing sufficient acid to insure an hydrogen ion concentration of not more than pH 3.0 until substantially free from metallic radicals, and then washing the thus purified fibrous alginic acid with pure water.

14. The process of preparing pure fibrous alginic acid from marine plants containing alginates which comprises leaching said marine plants with water to remove adherent and adsorbed salts inherent therein, comminuting the said plants and treating the same with a solution of sodium carbonate to form a solution of sodium alginate, filtering the cellular débris and insoluble matter from the said solution, precipitating calcium alginate from said solution by its admixture with a solution of calcium chloride, carrying out the said precipitation in a medium having an hydrogen ion concentration not below substantially pH 7.0, separating and washing the precipitated calcium alginate, liberating free fibrous alginic acid from said calcium alginate, washing the liberated fibrous alginic acid with water containing sufficient acid to insure an hydrogen ion concentration of said water of not more than pH 3.0 until said alginic acid is substantially free from calcium salts, and then washing the thus purified alginic acid with pure water.

15. In a process for preparing pure fibrous alginic acid, that step which comprises freeing the alginic acid from metallic radicals after its liberation from an insoluble alginate by treatment with water containing sufficient acid to insure an hydrogen ion concentration of said water of substantially from pH 2.5 to pH 3.0.

16. In a process for preparing an insoluble alginate in fibrous form, that step which comprises precipitating an insoluble alginate from a solution of a soluble alginate by metathesis with a metallic salt solution at a hydrogen ion concentration of from pH 10.5 to pH 11.0.

17. A process of preparing fibrous calcium alginate which comprises treating a calcium chloride solution having an hydrogen ion concentration substantially of from pH 10.5 to pH 11.0 with a substantially neutral sodium alginate solution.

18. A process of preparing fibrous alginic acid which comprises treating a fibrous insoluble alginate with a mineral acid to liberate alginic acid, washing the thus liberated alginic acid with acidulated water until it is substantially free from metallic radicals, and then washing the same with pure water to substantially remove said mineral acid.

19. That step in the process of treating kelp for the extraction of alginates to control the viscosity thereof consisting in storing the fresh kelp for some time prior to treatment thereof for extraction of the alginates and maintaining the normal moisture content of the kelp during such storing.

20. The process of controlling the viscosity of alginate solutions derived from fibrous alginic acid, which comprises treating the said alginic acid with dilute acids at temperatures from about 20° C. to about 50° C.

21. The process of controlling the viscosity of alginate solutions derived from fibrous alginic acid, which comprises treating said alginic acid with dilute acids at from 40 to 50° C.

22. The process of lowering the viscosity of alginate solutions derived from fibrous alginic acid, which comprises treating the said alginic acid with dilute mineral acid solutions, and carrying out said treatment at a temperature from about 20° C. to about 50° C.

23. The method of bleaching insoluble fibrous alginates which comprises treating the same with a solution of an alkali hypochlorite.

24. The method of bleaching insoluble alginates held in suspension in fibrous form which comprises treating the same with a solution of sodium hypochlorite.

25. The method of bleaching fibrous calcium alginate which comprises treating the same with a solution of sodium hypochlorite.

26. The process of producing bleached fibrous and substantially colorless pure alginic acid from marine plants containing algin, which comprises converting the alginic acid contained in said marine plants into a soluble alginate, thereupon precipitating an insoluble alginate from a solution of the said soluble alginate, bleaching said insoluble alginate with a hypochlorite solution, and then converting the thus bleached insoluble alginate into free alginic acid by treatment of said alginate with an acid.

27. The process of producing fibrous substantially pure and colorless alginic acid which comprises treating marine plants containing alginic acid compounds with an alkaline solution to produce a soluble alkali alginate, filtering said solution to remove cel-

lular débris and insoluble matter therefrom, adding said solution to a solution of a salt capable of forming an insoluble alginate to precipitate an insoluble alginate in a fibrous and filterable form, separating said precipitated insoluble alginate, washing the same, sludging the same up with a solution of a bleaching agent comprising a hypochlorite to bleach the same, washing the same with water, treating the same with an acid to liberate fibrous alginic acid therefrom, washing said liberated fibrous alginic acid substantially free from metallic salts, and then washing said alginic acid with pure water.

28. The process of treating fibrous alginic acid held in suspension, with dilute acids at temperatures above room temperature but not exceeding 50° C. for the purpose of controlling the viscosity of alginate solutions derived from said alginic acid.

29. The process of controlling the viscosity of alginate solutions derived from alginic acid which comprises treating the said alginic acid, prior to its conversion into soluble alginate and while in an insoluble fibrous form in suspension, with dilute acids at temperatures above room temperature but not exceeding 50° C.

30. The process of preparing substantially pure alginic acid salts which comprises neutralizing substantially pure fibrous alginic acid with metallic compounds capable of combining with said alginic acid with the concomitant production of alginic acid salts with water as the only by product.

31. Substantially neutral metal alginates substantially free from salts other than alginates.

32. Metal alginates prepared by neutralization of pure fibrous alginic acid with metal oxides and characterized by freedom from salts other than alginates.

33. Process for preparing pure alginates which comprises neutralizing pure fibrous alginic acid with metal oxides.

34. The process of preparing pure soluble metal ammonium alginates; which comprises treating a metal oxide with pure fibrous alginic acid to form an insoluble alginate, and thereupon treating said alginate with ammonium hydroxide.

35. The process of preparing substantially pure cuprammonium alginate; which comprises treating pure fibrous alginic acid with copper oxide to form insoluble copper alginate, and treating the said copper alginate with ammonium hydroxide.

36. The process of preparing pure cuprammonium alginate; which comprises treating pure fibrous alginic acid with copper oxide to form insoluble copper alginate, and treating the said copper alginate with ammonium hydroxide to form cuprammonium alginate.

37. The process of preparing copper alginate in a high state of purity; which comprises suspending fibrous alginic acid in water, adding copper oxide to said suspension and thereupon agitating said suspension until combination between the alginic acid and the copper oxide has taken place, and recovering the insoluble copper alginate from the suspension by known means.

38. The process of preparing substantially pure alginic acid salts; which comprises neutralizing substantially pure fibrous alginic acid with metal compounds capable of combining with said alginic acid to form alginates with the concomitant production only of water and carbon dioxide as by products.

39. Metal alginates prepared by neutralization of pure fibrous alginic acid with metal carbonates and characterized by freedom from salts other than alginates.

40. Magnesium alginate substantially free from salts other than alginates.

41. Process for preparing pure alginates; which comprises neutralizing pure fibrous alginic acid with metal carbonates.

42. The process of preparing pure magnesium alginate, which comprises preparing pure fibrous alginic acid free from metal radicals, and treating said pure alginic acid with magnesium carbonate.

43. The process of producing alginates in a relatively high state of purity and substantially free from foreign salts and impurities; which comprises suspending fibrous alginic acid in water, adding an insoluble metal carbonate to said suspension, agitating the suspension until reaction has taken place between the alginic acid and the insoluble carbonate with resultant formation of the metal alginates and the liberation of carbon dioxide from the said carbonate, and recovering the metal alginate thus formed from the reaction medium by known means.

44. The process of preparing pure cuprammonium alginate, which comprises treating pure fibrous alginic acid with copper carbonate to form insoluble copper alginate, and treating the said copper alginate with ammonium hydroxide to form cuprammonium alginate.

45. The process of preparing zinc-ammonium alginate, which comprises treating pure fibrous alginic acid with zinc carbonate to form insoluble zinc alginate, and treating the said zinc alginate with ammonium hydroxide to form zinc-ammonium alginate.

In witness whereof, we have hereunto subscribed our names.

FRED CURTIS THORNLEY.
MICHAEL J. WALSH.