

UNITED STATES PATENT OFFICE.

ALFRED WOHL, OF CHARLOTTENBURG, GERMANY.

PROCESS OF EXTRACTING SUGAR FROM ITS SOLUTIONS.

SPECIFICATION forming part of Letters Patent No. 707,889, dated August 26, 1902.

Application filed December 21, 1895. Serial No. 572,894. (No specimens.)

To all whom it may concern:

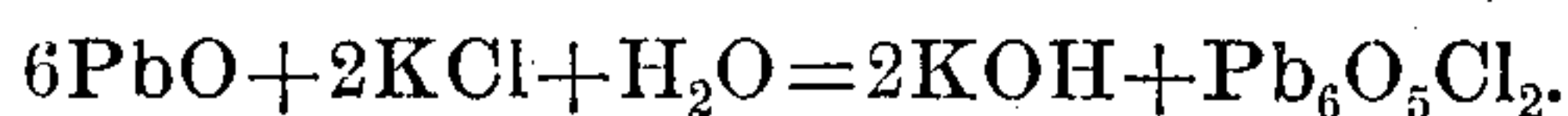
Be it known that I, ALFRED WOHL, doctor of philosophy, a subject of the King of Prussia, residing at Charlottenburg, near Berlin, in the Kingdom of Prussia, German Empire, have invented a new and useful Improved Process for Extracting Sugar from its Solutions, (for which I have obtained Letters Patent of Germany, No. 85,024, bearing date July 26, 1893; of France, No. 250,022, bearing date September 3, 1895; of Belgium, No. 113,387, bearing date November 16, 1895; of Great Britain, No. 22,859, bearing date November 29, 1895, and of Austria, No. 4,577, bearing date November 14, 1896;) and I do hereby declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the extraction of sugar from molasses and other impure after-products obtained in the manufacture of sugar; and it has for its object to operate this extraction in a simpler and more economical manner than heretofore. To this end the invention is based on the sucrate-forming property of lead protoxid, (PbO ;) and it consists in an improved process comprising the production and decomposition of the lead sucrate, as also the regeneration of the lead protoxid, for use in a new cycle of operations and the elimination of the last traces of lead from the solution obtained by the decomposition of the lead sucrate.

It is a well-known fact that sugar and protoxid of lead (PbO) will combine into a sucrate practically insoluble provided the lead protoxid be employed in a finely-divided state and maintained in intimate contact with the solution of sugar. This course has, indeed, been suggested before now by Dubrunfaut for the extraction of sugar from solutions; but neither Dubrunfaut nor any of the subsequent chemists have succeeded hitherto in obtaining a sufficiently complete separation of sugar by the agency of protoxid of lead. Especially this substance has failed in acting as a sugar-extracting agent when applied to molasses and similar impure products. It is by my investigations that the special conditions have been detected upon which depends a uniformly satisfactory formation

of lead sucrate and which therefore enable me to carry out Dubrunfaut's suggestion as a practically or commercially workable process. It is a well-known scientific fact that pure protoxid of lead (PbO) is obtainable in two modifications—viz., as red protoxid and as yellow protoxid. As to amorphous protoxid of lead, which is obtained by the oxidation of metallic lead or by heating white lead or nitrate of lead, it constitutes a mixture of those two modifications in varying proportions. Now I have found that these two modifications of lead protoxid present the following particularities as to their behavior toward sugar solution; approximately pure red protoxid (PbO)—for example, red flake litharge—when finely ground and sifted will act upon sugar solutions in an almost imperceptible way if unassisted by heat, its action being slow even in the case of fifty-per-cent. solutions, and so at the temperature considered as most favorable to such action—i. e., 80° to 90° centigrade—it is only by the use of an excess of sugar aided by a long digestion that pure red protoxid of lead is completely converted into lead sucrate. Yellow protoxid, however, (obtained, for example, by heating the same ground flake litharge for a short time at a temperature of 600° centigrade,) will “bind” sugar almost instantaneously and at an ordinary temperature provided other conditions are satisfactory. For this reason the said “yellow” modification may be distinguished by the term “active” protoxid. The inequality of the action on saccharine solutions of amorphous protoxid of lead, which is obtained by burning basic carbonate of lead, therefore results from the varying proportion in which the yellow and red modifications are present in a given case, according as the burning of the basic lead carbonate has been effected at a higher or lower temperature. Thus where the burning temperature does not exceed that which is required for eliminating the carbonic acid from the basic lead carbonate—say from 200° to 300° centigrade—scarcely anything but red protoxid is obtained. Where a dark-red heat is employed, (about 600° centigrade,) all the basic lead carbonate becomes converted into soft porous protoxid, which is as yellow as sulfur, and this protoxid is obtained in a per-

fectly pure condition by being rapidly cooled. In the latter form lead protoxid is most active as a sugar-extracting medium. By still further raising the temperature the yellow protoxid becomes harder and harder, until at cherry-red heat it will fuse. When subjected to compression—*i. e.*, when ground or triturated—the yellow lead protoxid will change to the red modification. This change may be met, however, by grinding the yellow protoxid in wet state, (“wet grinding,”) it being immaterial whether the protoxid is ground separately while being moistened with water and then mixed in the state of a thin pulp with the sacchariferous liquor or whether the grinding operation is performed in the liquor itself from which it is desired to extract the sugar and at the same time with the formation of the sucate. Considering that the yellow lead protoxid acts well at an ordinary temperature, no appreciable advantage is derivable from applying heat during the formation of the lead sucate where pure yellow protoxid is used; but where the lead protoxid available consists in a mixture of the yellow and red modifications part of the red modification will also be caused to combine with sugar by employing a higher temperature. On the other hand, the time taken up by the reaction depends upon the more or less extensive area of the “active surface”—that is to say, upon the greater or less excess of protoxid of lead employed and the fineness of its division. In the case of impure sacchariferous solutions, such as molasses and other impure after-products obtained in the manufacture of sugar, besides sugar also the non-saccharine bodies present—*i. e.*, the salts contained in the molasses, &c.—enter into reaction with the lead protoxid. This reaction mainly results in forming basic salts of lead, whereby alkali is liberated from said bodies. For instance, taking the potassium chlorid present in the molasses, &c., a reaction will take place according to the following equation:



Ordinary beet-root-sugar molasses, for example, will thus consume or absorb at least twenty per cent. of the yellow or active protoxid for every one hundred parts of molasses. Now I have ascertained that this useless consumption of lead protoxid may be almost wholly avoided by adding such an amount of free alkali to the solution as is required for raising the alkalinity of the liquor to the same or a higher degree as that to which it would rise in consequence of the reaction between the lead protoxid and the said non-saccharine bodies. The preventive effect of the addition of alkali is based upon the fact that basic lead salts are readily decomposed by a strong alkaline solution, so that if there is sufficiently free alkali added to the molasses, &c., any basic lead salt present will at once be redecomposed. From this it results that

the presence of a quantity of free alkali in the molasses, &c., as stated, will not allow basic lead salts to be formed or to subsist. This effect will be obtained by any alkaline agent, whether hydrated alkali, ammonia, alkaline earths, or alkaline carbonates. The most effective of these agents, sodium and potassium hydrates, will prove to be on account of their high coefficient of basicity; but potassium hydrate will be the more serviceable, as it does not prejudice the employment of the residuary lye for the extraction of potash, and it is recovered from the salin, together with that originally contained in the liquor, without occasioning any extra expense. As the basic nature of hydrated potash is very strong in comparison with that of protoxid of lead, comparatively small quantities of hydrated potash will suffice for excluding secondary reactions, so that the lead protoxid employed is utilized for the formation of lead sucate in a very thorough and complete manner, so as to render unnecessary any considerable excess of that agent. The increased purity of the lead sucate thus obtained affords the additional advantage of facilitating regeneration of the lead protoxid, which is recovered in a purer state, while, on the other hand, the increased alkalinity of the sugar solution becomes in itself a means of accelerating the formation of lead sucate. Experiments made with pure-sugar solutions have shown that where small quantities of alkali—say from five to twenty cubic centimeters of normal potash or soda-lye for every one hundred grams of sugar—were added, the temperature not being unduly raised, the sugar would be bound and separated out of its diluted solutions more rapidly and completely than it would without any such alkaline addition; but whereas pure lead sucate in consequence of such additional alkali is separated out in a state of such fine division that the slimy precipitate is scarcely capable of being filtered, this somewhat serious drawback does not make itself felt where the saccharine liquor (molasses, &c.) is less pure. The results of experiment, as above summarized, show that what is essential above all to a satisfactory yield of lead sucate from sacchariferous solutions treated with protoxid of lead (PbO) is that a protoxid should be employed which contains as large a proportion of the yellow or active modification as possible. Very concentrated solutions of molasses—that is to say, molasses which is thinned with one or two parts of water for every one part of molasses—both at ordinary and comparatively high temperatures, either with or without alkaline additions, may by such means be completely freed from the sugar they contain in a very short time provided that the surplus quantity of protoxid of lead employed is sufficiently large. More diluted solutions—that is to say, molasses which is thinned with not more than three parts of water for every one part of molasses—will give equally satisfac-

tory results, but only so long as the reaction is allowed to take place at normal or but a slightly-raised temperature, which in no case should exceed 70° or 80° centigrade, and where, moreover, alkali is added. The reason for restricting the temperature to the limit stated is dictated by the experience that the formation of lead sucrate is the more retarded by the presence of water the higher the temperature of the mixture.

In the case of ordinary beet-root-sugar molasses I employ from one to two per cent. of potassium hydrate (KOH) and seventy-five per cent. of active lead protoxid for one hundred per cent. of molasses, and this without any heating is sufficient to cause the whole of the sugar to be so completely converted into lead sucrate in a space of two hours that a lævorotary liquor results. Where eighty per cent. of active lead protoxid is used, this effect is obtained in about one hour's time. Where the proportion is increased to ninety per cent., it will be obtained in less than half an hour, and at one hundred per cent. within five minutes, or rather under. This result may be obtained, too, with seventy per cent. of active lead protoxid if the mixture after being well stirred is allowed to stand at rest for from ten to fifteen hours at the ordinary temperature. Theoretically the quantity of active lead protoxid requisite for the formation of bisucrate of lead is one hundred and thirty-three and one-third per cent. of the quantity of sugar to be transformed. For instance, if the molasses contain fifty per cent. of sugar the percentage of active lead protoxid would have to be sixty-six and two-thirds per cent. Where the lead protoxid has not been properly burned—being, for example, too hard, or having still retained a deep yellow color—there will be a reduction of the effect amounting to twenty per cent. or more, according as more or less red protoxid is present. The dilution of the sucrate for the purpose of accelerating filtration is preferably effected with a quantity of warm water sufficient to produce a pulp-like mass capable of running at a temperature of from 40° to 50° centigrade. For washing first water at from 40° to 50° should preferably be used and then the temperature raised by slow degrees, so that the filtered liquor is finally collected at from 70° to 75° centigrade. By these means the lixiviation is very considerably accelerated without any loss or waste, the fact being that lead sucrate will scarcely dissolve in water even with the assistance of heat. In alkaline lyes, however, such as are obtained by additions of alkali or simply by the action of protoxid of lead upon impure solutions of sugar, such as molasses, &c., experiment has shown that the solubility of sucrate of lead is small at temperatures under 60° centigrade, only a quantity of lead sucrate corresponding to about 0.1 to 0.15 per cent. of sugar being dissolved. When the temperature exceeds 60° centigrade, the quan-

tity of lead sucrate that is dissolved rapidly increases, keeping pace with the rise of the temperature, so that in such an emergency considerable losses of sugar might take place. It is obvious that these losses can be avoided by removing the greater part of the alkali by washing.

For the purpose of extracting the sugar from the lead sucrate the latter is treated with carbonic acid or subjected to carbonation, care being taken to cause a close contact between the gaseous acid and the sucrate by providing suitable mechanical devices, such as metallic strainers inserted into the saturating-pans, means for stirring up the precipitate from the bottom, and the like. The carbonation should be effected at ordinary temperature or at a temperature not higher than 70° to 80° centigrade and discontinued as soon as the polarizing power of the liquor ceases to be increased. I have found that the absorption of the carbonic acid is greatly facilitated in the beginning of the operation by diluting or stirring the washed sucrate with a sugar solution instead of water. Such solution may, for instance, consist in the filtered liquor resulting from a previous carbonation, or it may even consist in an impure solution, such as molasses or juices, which will thereby be purified, provided the proportion of same be such that there is an excess of lead sucrate. The sugar solutions obtained by the carbonation of the lead sucrate until the whole of the sugar has been separated are perceptibly colored a brown hue by the addition of sulfureted hydrogen after the separation of the precipitate, or, in other terms, the solubility of the carbonate of lead in a sugar solution, which may be represented by the proportion of one to fifty thousand for a twenty-per-cent. solution, is too great for the present purpose, but under certain suitable conditions that solubility may be reduced to zero by the presence of dissolved carbonate of lime. Pfeiffer and Langen have shown before now that by repeatedly treating diluted sugar solutions containing lead with lime and carbonic acid the proportion of lead contained in such solutions is greatly reduced, so that in the sugar separated from the solution in the condition of sucrate of lime mere traces of lead can be detected. I have found since that the solubility of carbonate of lead in sugar solutions in the presence of carbonate of lime will be the more reduced the higher the temperature and the higher also the degree of concentration of the sugar solution, but invariably to a very great extent. Sacchariferous solutions, no matter of what degree of concentration—say 20°, 33°, or 50° Brix—from which the main portion of the lead has been separated by means of carbonic acid by being treated once with about one to one-half of a part of lime to one hundred parts of sugar and with carbonic acid and filtered at a temperature of 80° to 90° centigrade, will be freed from lead

to such an extent that no further reaction can be observed when the solution is first mixed with acetic acid and then treated with sulfureted hydrogen, though in a fifty-per-
 5 cent. solution that has not been treated as stated sulfureted hydrogen will detect one part of lead to twenty million parts of solution or to ten million parts of sugar. Under such conditions—viz., the employment of con-
 10 centrated solutions and comparatively high temperatures—the solubility of the carbonate of lead in sacchariferous solutions in the presence of carbonate of lime is therefore many times less than the solubility of any
 15 one of the least soluble compounds in water, (BaSO_4 1:430,000, &c., up to AgBr 1:2,000,000.) Accordingly, with a view to the total elimination of all traces of lead, the liquor separated by filtration from the lead precipitate is sub-
 20 jected after concentration to from 40° to 50° Brix to a defecating process in the presence of one-fourth to one-half part of calcium hydrate (CaH_2O_2) for every one hundred parts of sugar present and at a temperature at from
 25 80° to 90° centigrade, after which the liquor is separated from the small quantity of precipitated matter by filtration at a high temperature. I have also ascertained that a further method for the reliable elimination of the
 30 least traces of lead there may be left consists in heating the concentrated solutions with animal charcoal, used in the proportion of from one to two parts for every one hundred parts of sugar, or with very small quantities
 35 of magnesium powder—say from one to two grams for every one hundred kilograms of sugar. The subsequent use of either of these two mediums suffices to obviate even the remotest possibility of any traces of lead re-
 40 maining in suspension in the fluid in consequence of any leakage in the filtering-press or of their finding their way into the solution accidentally at any subsequent period. Es-
 45 pecially where charcoaling is used not only is every trace of any lead salt that may by any chance have been dissolved greedily absorbed, but in addition to this a perfect mechanical clarification is obtained with certainty.

Example: Six hundred kilograms of soft
 50 sulfur-yellow lead protoxid are uniformly ground in a mill, preferably a vertical mill, together with four hundred liters of water during from ten to fifteen minutes. Then eight hundred kilograms of molasses, four hundred
 55 liters of water, and twenty-five liters of "technical" potash lye having fifty per cent. of potassium hydroxid are added and thoroughly stirred and mixed for another ten or fifteen minutes until the mass begins to
 60 thicken. Then the latter is drawn off into reservoirs so long as it is capable of running and is here left for from an hour and a half to two hours. Within this time the lead sucrate will have become a viscid mass and
 65 the reaction will be complete. The sucrate is then removed from the receivers and mixed with a small quantity of hot water—say from

one-half to one part of water to one hundred parts of molasses—and the thick semiliquid mass thus obtained, the temperature of which
 70 should preferably not exceed from 40° to 50° centigrade, is filtered by means of a filtering-press and then washed with water, which in the beginning should be not hotter than from
 75 40° to 50°, but then should be applied with a higher temperature. The mill may be charged with a fresh supply of material directly the preceding charge has been removed. The washed sucrate is first diluted by stirring it
 80 with water, or more advantageously with a saccharine solution, and then treated with carbonic acid until the polarizing power of the liquor ceases to be increased, when the latter is separated from the precipitate by filtration. The precipitate, which mainly consists of
 85 basic carbonate of lead, is transformed into yellow lead protoxid in any convenient manner to reuse the latter in a following operation. The saccharine solution is purified from the last traces of lead as described or in
 90 any other known manner and finally worked as usual.

What I claim is—

1. The process for extracting sugar from molasses and other impure after-products ob-
 95 tained in the manufacture of sugar, which consists in mixing molasses with a watery solution of an alkali oxid, stirring the mixture together with finely-ground protoxid of lead, allowing the mixture to stand until a viscous
 100 mass has formed, and washing with water, substantially as and for the purpose stated.
2. In the process for extracting sugar by the agency of lead protoxid from molasses and other impure after-products obtained in the
 105 manufacture of sugar, the method of freeing the lead sucrate from the adhering impurities by diluting the sucrate with water of a temperature of 40° to 50° centigrade, filter-pressing and washing the contents of the fil-
 110 ter-press first with water of 40° to 50° centigrade and then with water the temperature of which is gradually raised to 70° to 75° centigrade, substantially as and for the purpose stated.
3. In the process for extracting sugar by the agency of lead protoxid from molasses and other impure after-products obtained in the
 115 manufacture of sugar, the method of removing the last traces of lead from the sugar liquor obtained by the carbonating process, which consists in concentrating the sugar
 120 liquor, adding one-fourth to one-half per cent. of calcium hydrate, treating with carbonic acid at a temperature of 80° to 90° cen-
 125 tigrade, and separating the liquor from the precipitate, substantially as described.
4. The process for extracting sugar from molasses and other impure after-products ob-
 130 tained in the manufacture of sugar, which consists in mixing the molasses, &c., in the presence of not more than three parts of water for every one part of molasses, &c., with an excess of lead protoxid as free as possible

from the red modification of lead protoxid, adding a hydrated alkali; allowing the mixture to stand at ordinary temperature until a homogeneous viscous mass has formed containing the sugar in the form of lead sucrate, thinning the mass with water having a temperature of 40° to 50° centigrade, filter-pressing the same, washing the contents of the filter-press with water having an initial temperature of 40° to 50° centigrade which is then gradually raised up to 70° to 75° centigrade, decomposing the washed lead sucrate, separating the precipitate from the sugar liquor,

concentrating the liquor, adding one-fourth to one-half per cent. of calcium hydrate, carbonating at a temperature of from 80° to 90° centigrade, and filtering, substantially as described. 15

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses. 20

ALFRED WOHL.

Witnesses:

GEORG WEHMKE,
HANS PLÖTZ.