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METHOD OF POLISHING CRYSTAL GLASS AND
LEAD CRYSTAL GLASS ARTICLES

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Polishing of articles made of crystal glass and in particular of lead crystal glass has hitherto been effected with the aid of aqueous sulphuric acid containing hydrofluoric acid, in wide-meshed baskets consisting of copper or plastic material. The baskets filled with the articles to be polished are first moved uniformly in the polishing bath, thereafter removed from the polishing bath and dipped into a warm water bath. In this water bath the reaction products which have been formed in the polishing bath and which adhere to the glass surface are washed off. It is necessary to repeat these steps very often until the desired gloss or polish is obtained on the surface and on the ground edges of the articles.

In practicing this method it cannot be avoided that considerable amounts of water originating from the washing bath are transferred into the polishing bath and that the concentration and the effect of the polishing bath are thereby reduced in the course of the polishing process. Therefore, it is necessary to restore the polishing bath from time to time to a state of optimum concentration by adding either hydrofluoric acid or sulphuric acid or both, taking into account, however, that the volume of the polishing bath increases considerably while the operation proceeds. Under these circumstances considerable amounts of the liquid from the polishing bath must be removed at certain time intervals and discharged or worked up as waste acid, respectively. Subsequently the bath must be renewed, which means that there is a relatively poor degree of utilization of the hydrofluoric acid and the sulphuric acid and, in consequence there is considerable acid consumption.

Working up waste acids which have a high concentration and contain fluorine compounds involves considerable difficulties and costs, which is the reason why diluted waste acid is frequently discharged into rivers. These are technological as well as commercial disadvantages of the known polishing methods. The hydrofluoric acid and sulphuric acids contained in the large quantities of washing water are likewise lost.

The present invention relates to a method of polishing glass articles, made in particular of crystal glass having at least a lead oxide content of 23% and lead crystal glass, such as fancy glass, luxury glass articles, glass ware, imitation stones, mirrors, glass chandeliers, optical glasses and the like, by which the difficulties and disadvantages of the known polishing methods are not encountered and by which perfectly polished glass articles may be obtained in a very economical manner and without any necessity for costly processes for working up waste products.

The inventive method uses—in a per se known manner—sulphuric acid containing hydrofluoric acid as the polishing bath whose content of hydrofluoric acid is from about 5 to 10%. In the course of this chemical polishing process a deposit of salt-like reaction products is formed on the glass surface which are one or more compounds of the group comprising compounds of the cations of the glass, fluoro compounds, silicates, sulphates and the like. However, since there is a rapid reduction of the polishing effect of the polishing bath while the thickness of the deposit increases, the deposit must be removed after each immersion in the polishing bath.

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According to the inventive method this deposit is not, however, washed off with water as in accordance with the known methods, but the articles coated with the reaction products are dipped into a sulphuric acid bath which has such a high concentration of sulphuric acid that the acid has a dewatering or dehydrating effect. Therefore, it is an essential feature of the invention that the sulphuric acid used has a concentration of at least 66% which corresponds approximately to the stage of the eutectic of the tetrahydrate and dihydrate of sulphuric acid. The effect aimed at by the invention is obtained only by using a sulphuric acid which shows such a high degree of hygroscopicity that it separates water from the deposit of the reaction product by destruction of the salt crystals and decomposition of the fluorine and silica-containing compounds.

The porous coating of reaction products on the surface of the glass contains various sulphates, silicates and the like. It also contains small amounts of hydrofluoric acid originating from the polishing bath. This hydrofluoric acid is reacted in the relatively highly concentrated sulphuric acid bath in the presence of silicic acid or silicates to form silicon tetrafluoride or hydrogen fluoride or other volatile fluoro compounds or several of the afore-mentioned compounds which escape in the form of gases and separate the film of reaction products adhering to the glass surface from the said glass surface.

This separation is additionally promoted by other reactions in the salt coating which result from the dehydrating effect of the highly concentrated sulphuric acid. The result obtained is that the salt deposit peels off the article to be polished in the sulphuric acid bath without washing, so that the glass article may be dipped again into the polishing bath and need not be rinsed any more with water after each working cycle, as it had been necessary in connection with the known methods.

A quite essential advantage of the inventive process can be seen in the fact that by using highly concentrated sulphuric acid as the second bath virtually no water which has not dripped off the surface to be polished is introduced or transferred into the polishing bath when the articles are immersed again—which would gradually lead to a considerable dilution of the polishing bath—so that the concentration can be maintained at a constant level over very long periods of operation.

It is a further advantage of the inventive method that avoiding the continuous dilution of the polishing bath by water from the washing bath which adheres to the glass articles eliminates a discharge of waste acid and any problems involved, in particular the problems of neutralizing the acids and processing the fluoro compounds contained in the waste water. In case of long periods of operation there is merely a relatively small increase in the volume of the polishing bath which is due to the transfer of sulphuric acid which has not dripped off the glass articles from the second bath into the polishing bath. The resulting reduction of the concentration of the hydrofluoric acid can be easily compensated by adding highly concentrated hydrofluoric acid, e.g., with a hydrogen fluoride content of 90% or more, or anhydrous hydrofluoric acid, or fluoro-sulphonic acid. Consequently, there will be waste acid in an amount corresponding to this increase in volume and to the quantity added to make up the hydrofluoric acid content. The amounts of waste acid produced by the present method are, of course, extremely small as compared to those continuously obtained according to the known methods.

The vapors escaping from the second bath, i.e., the salt removing bath which contain fluoro compounds, such as, e.g., silicon tetrafluoride and hydrogen fluoride

can be drawn off and purified by appropriate absorption plants. In this way the proportion of fluoro compounds can be recovered. In the aforementioned vapors almost the whole content of fluoro compounds consumed from the polishing bath is present. The hydrofluoric acid regenerated in the conventional manner can be recycled into the polishing bath.

In practicing the inventive method it should be observed that the temperature of the polishing bath should be maintained in a range between about 40 and 60° C. A higher temperature is unsuitable since otherwise the loss of hydrofluoric acid because of the considerable vapor pressure which the said acid assumes at higher temperatures becomes too large and the glass surfaces might even be etched.

The appropriate temperature of the second bath, i.e., of the salt removing or sulphuric acid bath, is about 60° C. or slightly more. At this temperature the fluoro compounds transferred from the polishing bath evaporate and escape quickly and completely, which is an object of the invention. The viscosity of the highly concentrated sulphuric acid is very high, but has already been reduced to such an extent at this elevated temperature that the bath liquid originating from the second bath runs off the articles quickly and that the amount of sulphuric acid transferred from the salt removing bath into the polishing bath is relatively small. This amount corresponds approximately to the amount of sulphuric acid consumed to form the sulphates present in the salt deposit on the glass surface in the polishing bath.

It has turned out to be useful to heat the two baths, i.e., the polishing bath and the sulphuric acid bath, independently of each other and to maintain the temperature of the sulphuric acid bath in a range which is by 10 to 20° C. higher than the temperature prevailing in the polishing bath. This measure does not only have the effect of facilitating the separation of the salt deposit by the rapid change of the temperature of the articles transferred from one bath into the other, but also allows to control operation in a way such that the amount of sulphuric acid transferred with the articles from the sulphuric acid bath into the polishing bath is just sufficient to make up the sulphuric acid content of the polishing bath.

It is understood that the reduction of the sulphuric acid content of the polishing bath can be easily ascertained in the usual way. Accordingly, the temperature of the salt removing bath is adjusted since it is possible by varying the bath temperature to change the viscosity of the sulphuric acid and the amount of liquid which does not drip off the articles within a specific period. By means of appropriate operating conditions which can be controlled and adjusted in a very simple way by temperature selection the working capacity of the two baths can be maintained over a very long period of time without any or with a minimum of additions only for keeping the concentration at a constant level.

The appropriate polishing bath consists of an aqueous sulphuric acid of a medium concentration, such as, e.g., sulphuric acid of a concentration of from 50 to 60%, containing hydrofluoric acid in an amount preferably from 5 to 7%. The hydrofluoric acid can be admixed as such or in the form of fluoro-sulphonic acid with the sulphuric acid in accordance with any known technique.

A reduction of the concentration of the second bath which may occur after a long period of operation is conveniently compensated—an increase in volume being simultaneously avoided—by adding fuming sulphuric acid (oleum) or highly concentrated sulphuric acid (having a concentration of from 96 to 98%) or both or by heating both to a temperature between 110 and 150° C. for a period of 1 to 2 hours to remove water vapor.

The reaction products originating from the polishing

bath which peel off the glass surface in the second bath under the dehydrating effect of the sulphuric acid, the effect of the escaping gases formed and under the influence of the sudden change of temperature are substantially or to a large extent insoluble in the highly concentrated sulphuric acid and sink to the bottom. The reaction products peel off to such a large extent that a specific cleaning process, such as, e.g., by washing with water, is not required before the articles are immersed again in the polishing bath. If there is a considerable enrichment of the sulphuric acid bath with salts after some time, the salt can be separated in a simple manner by cooling the bath to 0° C. or below, for instance to -10° C. After this regeneration of the sulphuric acid contained in the salt removing bath, the salt contents of the sulphuric acid bath are below 0.1% in general.

When the articles have been dipped into the polishing bath and subsequently immersed in the sulphuric acid bath repeatedly and if the desired polish has been obtained on the surfaces and on the edges, the articles must be rinsed with water but once and can be dried. After this procedure the articles are ready for use and show high polish and bright gloss, without any subsequent treatment being necessary.

If there is an enrichment of the polishing bath with salts, i.e., with the reaction products removed from the glass surface, the polishing effect of the bath becomes incomplete according to the known methods. In addition to that, the salt deposits on the glass surfaces can be separated or washed off to a very small extent only or not at all in the conventional water washing baths which are used in connection with the known methods. Consequently, the polishing treatment is disturbed.

In contradistinction to that, separation of the salt deposits on the articles is accomplished by the inventive sulphuric acid baths if the polishing bath has been completely saturated with the reaction salts. Moreover, the reaction is neither inhibited nor retarded, which would lead to an extension of the polishing time or to a discontinuation of the polishing effect of the polishing bath. Therefore, a renewal of the polishing bath because of this enrichment with salt which necessarily implies a renewal in the case of the known methods, is not required in connection with the inventive method.

A comparison between the consumption of acids by the known methods and by the inventive method shows that the procedure according to the invention saves 80 to 85% of sulphuric acid and 45 to 60% of hydrofluoric acid and produces waste acid in an amount of 5% only unless fuming sulphuric acid is used for regenerating the sulphuric acid or a concentration of the sulphuric acid is effected by means of water evaporation, as compared with the conventional polishing methods.

Moreover, it was found surprisingly that a salt deposit is formed which adheres so weakly to the glass surface that it peels off to a large extent already while the articles are moved in the polishing bath if various heavy metal salts of the kind used in mechanical polishing processes for improved wetting preferably iron chloride, iron sulphate, zinc sulphate, copper sulphate, silver sulphate or potassium permanganate, chromic acid or hydrogen peroxide are added to the polishing bath. On account of this fact it is possible to obtain a considerably improved polishing effect by an individual immersion in the polishing bath since the salt deposit of increasing thickness does not as strongly affect the polishing reaction. Consequently, the number of alternating treatments or working cycles comprising immersion in the polishing bath and in the sulphuric acid bath can be reduced considerably. It is even possible in extreme cases to obtain a sufficient and perfect polish by a single working cycle of this kind. The mode of action of the afore-mentioned additions has not yet been fully clarified, but it can be assumed that the additions produce surface effects and activation phe-

nomena. In this connection the surface tension appears to be of some importance.

It is obvious that the reduction of the number of alternating treatments required by this embodiment of the inventive method shows additional important advantages of a commercial nature. The expenditure for drawing off and working up the fluoro-containing vapors from the sulphuric acid baths and for regenerating the fluoro compounds for reutilization in the polishing bath has been reduced to a minimum, the capacity of polishing baths available is considerably increased, utilization of the acids present in the polishing bath and in the sulphuric acid bath is improved and in case of proper operation the concentration of the two baths can be maintained at an optimum level without any additional specific process steps.

Although it was known in connection with the mechanical polishing of glass surfaces to add metal salts of this kind to the polishing composition, it was not possible to draw any conclusions applicable to the dip polishing method since there are no parallels between mechanical polishing and the suspensions used therefor and the method of chemically polishing articles with the aid of a sulphuric acid containing hydrofluoric acid.

The proportion of heavy metal additions to be used depends on the composition and the surface of the glass articles to be treated. Also the kind of polish desired be taken into account. If very high concentrations of additions are used, very sharp-edged contours are obtained which require a minimum of working cycles. Actually, a treatment in the sulphuric acid bath is necessary in this case only in order to polish also those parts of the articles which are contacting each other or touch the containers.

If lower concentrations of the above-mentioned additions are used, the edges obtained are not as sharp and the polish corresponds much more to the polish obtainable by the conventional technique. The number of alternating treatments in the polishing bath and the sulphuric acid bath decreases in general in response to the increasing concentration of additions. Therefore, it is possible in principle to obtain the desired degree of polish already by a single immersion in the polishing bath, but it is extremely difficult in such a case to control the polishing process, so that it will be advisable in practice to work with lower concentrations of additions and, in consequence, with more frequent alternating treatments. After the final immersion in the polishing bath the articles are dipped as before into the sulphuric acid bath in order to remove the remiander of the salt deposit, subsequently rinsed in the water bath in order to remove remaining acid and thereafter dried.

The inventive method will be illustrated in detail by means of the following examples which are not meant to limit the scope of the invention. Any amounts of sulphuric acid and hydrofluoric acid stated in percent are statements in percent by weight.

Example 1

Three acidproof, separately heatable vessels were used which were arranged side by side and provided with a suitable hood for drawing off the vapors. The first vessel contained the polishing bath in the form of sulphuric acid of a concentration of 55% and hydrofluoric acid present in an amount of 5%. The second vessel contained the sulphuric acid bath in the form of sulphuric acid of a concentration of 67%. The third vessel contained water and served for rinsing the polished articles after the termination of the whole polishing process. The polishing bath and the sulphuric acid bath were kept at a temperature between 59 and 60° C. and the water bath was maintained at about 40° C.

The articles which were crystal glasses with a lead oxide content of at least 23% were immersed in the polishing bath and moved until the known salt deposit appeared on the surface. The deposit formation took an average time

of from 10 to 20 seconds. The articles were then removed from the polishing bath, allowed to drip, immersed and moved in the sulphuric acid bath. The salt deposit peeled off the glass surface in the concentrated sulphuric acid within a period of from 3 to 5 seconds. The articles were thereafter removed from the sulphuric acid bath, allowed to drip and immediately dipped again into the polishing bath.

The whole process was repeated several times, depending on the kind of glass to be polished. In general 10 to 18 cycles of treatment in the polishing and sulphuric acid baths were sufficient. After the final immersion in the sulphuric acid bath the articles were dipped into the washing water bath in the third vessel in order to wash off the adhering sulphuric acid.

Example 2

Three acidproof, separately heatable vessels were used which were arranged side by side and were provided with appropriate hoods for drawing off the waste gases. The first vessel contained the polishing bath which consisted of sulphuric acid of a concentration of 55% and hydrofluoric acid present in an amount of 5% and had a temperature of 50° C. The second vessel contained sulphuric acid of a concentration of 68% as the salt removing bath which was maintained at a temperature between 60 and 65° C. The third vessel again was filled with water and served for rinsing the finished articles.

Crystal glasses with a lead oxide content of at least 23% and of complicated shapes were immersed and moved in the polishing bath for a few seconds. Then the container having the shape of a wide-meshed copper basket containing the glasses was removed from the polishing bath, allowed to drip for a short period of time and subsequently dipped into the sulphuric acid bath. After the glasses had been moved for a few seconds in the sulphuric acid bath, the basket was removed and allowed to drip. These steps were repeated 12 times and the finally poished articles freed of adhering sulphuric acid in the third vessel, i.e., in the water bath, and dried.

Example 3

Three acidproof, separately heatable vessels were used which were arranged side by side and provided with appropriate hoods for drawing off the waste gases. The first vessel contained the polishing bath which consisted of sulphuric acid of a concentration of 52% and hydrofluoric acid present in an amount of from 2 to 3% and had a temperature of 55° C. The second vessel contained sulphuric acid of a concentration of 67% as the salt removing bath which was maintained at a temperature between 55 and 60° C. The third vessel again was filled with water and served for rinsing the finished articles.

Flashed crystal glasses with a lead oxide content of at least 23% having a very thin colorless glass coating were immersed and moved in the polishing bath for a few seconds. Then the container having the shape of a wide-meshed copper basket containing the glass was removed from the polishing bath, allowed to drip for a short period of time and subsequently dipped into the sulphuric acid bath. After the glasses had been moved in the sulphuric acid bath for a few seconds, the basket was removed and allowed to drip. These steps were repeated 12 times and the finally polished articles freed of adhering sulphuric acid in the third vessel, i.e., in the water bath, and dried.

Example 4

Three acidproof, separately heatable vessels were used which were arranged side by side and provided with appropriate hoods for drawing off the waste gases. The first vessel contained the polishing bath which consisted of sulphuric acid of a concentration of 55% and hydrofluoric acid in an amount of 5% and had a temperature of 55° C. In addition to the afore-mentioned components the polishing bath contained iron chloride which had been

introduced into the bath either in solid form or in the form of a saturated solution. The salt content, i.e., the content of iron chloride, of the polishing bath was 8%. The second vessel contained sulphuric acid of a concentration of 67% as the salt removing bath which was maintained at a temperature of 68° C. The third vessel again was filled with water and served for rinsing the finished articles.

Glasses were immersed and moved in the polishing bath for a few seconds. Then the container having the shape of a wide-meshed copper basket containing the glasses was removed from the polishing bath, allowed to drip for a short period of time and subsequently dipped into the sulphur acid bath. After the glasses had been moved for a few seconds in the sulphuric acid bath, the basket was removed and allowed to drip. These steps were repeated 5 times and the finally polished articles freed of adhering sulphuric acid in the third vessel, i.e., in the water bath, and dried.

Example 5

Three acidproof, separately heatable vessels were used which were arranged side by side and provided with appropriate hoods for drawing off the waste gases. The first vessel contained the polishing bath which consisted of sulphuric acid of a concentration of 58% and hydrofluoric acid in an amount of 7% and had a temperature of 60° C. In addition to the afore-mentioned components the polishing bath contained iron sulphate which had been introduced into the bath either in solid form or in the form of a saturated solution. The salt content, i.e., the content of iron sulphate, of the polishing bath was 15%. The second vessel contained sulphuric acid of a concentration of 69% as the salt removing bath which was maintained at a temperature of 70° C. The third vessel again was filled with water and served for rinsing the finished articles.

A suitably suspended crystal glass jug was immersed and moved in the polishing bath for a few seconds, then removed from the polishing bath, allowed to drip for a short period of time and subsequently dipped into the sulphuric acid bath. After the jug had been moved for a few seconds in the sulphuric acid bath, it was removed and allowed to drip. These steps were repeated 3 times and the finally polished jug freed of adhering sulphuric acid by rinsing with water and dried.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method of polishing glass articles, made in particular of crystal glass, comprising the steps of packing the glass articles into a wide-meshed container, immersing and moving the container filled with the articles to be polished in a vessel containing a polishing bath until a deposit of salt-like reaction products has been formed on the surfaces of the articles to be polished, the polishing bath consisting of a solution of sulphuric acid of a concentration of from 50% to 60% by weight which contains hydrofluoric acid in an amount of from 5 to 10%

by weight and is maintained at a temperature in the range between 40° and 60° C. thereafter removing the container with the articles to be polished from the polishing bath as soon as said articles have been coated with a salt deposit on their surfaces, immersing and moving said container in a vessel containing a salt removing bath until the salt deposit has separated from the surfaces of the articles, said salt removing bath consisting of a solution of sulphuric acid of a concentration of at least 66% by weight which is maintained at a temperature of at least 60° C., whereby the salt removing bath is maintained at a temperature in a range about 10 to 20° C. higher than the temperature of the polishing bath, removing the container with the articles to be polished from the salt removing bath as soon as said articles have been freed of the salt deposit, and repeating the alternating treatment in the polishing bath and in the salt removing bath until the desired polish has been obtained, whereupon the finally polished articles contained in the wide-meshed container are washed with water after the final treatment in the salt removing bath and dried.

2. The method according to claim 1 wherein additives are added to said polishing bath selected from the group consisting of heavy metal salts, potassium salts, potassium permanganate, chromic acid and hydrogen peroxide.

3. The method according to claim 1 wherein said polishing bath consisting of a sulphuric acid solution of a concentration of from 50 to 60% by weight contains hydrofluoric acid in an amount from 5 to 7% by weight and an additive selected from the group comprising iron salts, iron chloride, or iron sulphate in an amount of from 8 to 15% by weight and is maintained at a temperature between 40 and 60° C.

4. The method in accordance with claim 1 further comprising the step of making up the polishing bath to a hydrofluoric acid content of from 5-10% by weight by adding hydrofluoric acid in highly concentrated or anhydrous form, if there has been a reduction of the hydrofluoric acid content of the polishing bath.

5. The method according to claim 4, further comprising the step of making up the polishing bath to a hydrofluoric acid content of from 5 to 10% by weight by adding fluoro-sulphonic acid, if there has been a reduction of the hydrofluoric acid content of the polishing bath.

6. The method according to claim 1, wherein said polishing bath consists of a dehydrating sulphuric acid of a concentration of at least 66% by weight.

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