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POLISHING COMPOSITION AND PROCESS OF FORMING SAME

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This invention relates to improved polishing compositions and methods of forming these compositions, the same being adapted for use in polishing glass or glass-like materials, such as ophthalmic lenses, television tubes, mirrors, plate glass, etc. More specifically, the invention is directed to new and improved polishing compositions and methods of preparing the same, which compositions exhibit increased polishing speeds, and as incidental added benefits, materially slower settling rates, and improved redispersion characteristics.

A number of different chemical compounds, principally metal oxides, are used as polishing materials in the polishing of glass. These materials include red rouge (iron oxide), zirconium oxide, cerium oxide, and rare earth oxide. To be suitable as a polishing material, the compound should have a number of desiderata, the relative importance of each compound depending on the method of use thereof as well as the type and extent of polishing desired. Generally for commercial use, it is considered desirable for the polishing material to function relatively rapidly and economically in bringing the ground surface of the glass to the desired polished condition. While exceptions exist in connection with precision polishing of optical parts, it nevertheless is generally true that fast polishes are more desirable for economy of operation. Polishing speed is one factor of particular importance but the polishing material or composition should also produce an acceptable surface. Furthermore, the polishing compositions should exhibit good suspension properties with respect to dispersion retention and redispersibility after settling.

The speed of a polishing material may be rated on its relative ability to abrade glass. A suitable speed test consists of measuring the rate of removal of glass from a glass blank subjected to polishing in a standard ophthalmic machine. As polishing composition concentration and polishing pressure operation factors are involved, the usual practice is to set these at certain arbitrary values and to express the polishing speed of an unknown composition relative to a standard material measured under the same conditions. A suitable standard polishing material is cerium oxide which may be given a relative rating of 10.0 in connection with its polishing speed. This rating corresponds to the removal of 0.00394 gm./minute from a 55 mm. plano lens polished on a 4 inch felt lap revolving at 450 r.p.m. in a Premier or similar type ophthalmic machine with the lens being held against the felt at a pressure of 0.2 kg./cm.^{2} and at a polishing composition slurry concentration of 5% solids. The following are typical ratings of the polishing speeds of conventional polishing materials, the ranges indicating the results obtained from the testing of many samples from various lots of the specific materials.

Cerium oxide	9.5 to 12.0
Rare earth oxide	8.0 to 10.0
Zirconium oxide	4.0 to 7.0
Rouge	5.0 to 7.0

It is an object of the present invention to provide new and improved polishing compositions which exhibit increased polishing speeds as well as good dispersion retention, redispersion and non-caking characteristics.

A further object is to provide new and improved polishing compositions including therein the combination of a polishing material and materials which combine to provide a gelatinous ceric hydroxide or other gelatinous material, the composition in slurry form exhibiting improved polishing and slurry retention characteristics.

Still a further object is to provide a new and improved polishing composition which may be prepared, stored and shipped as a dry mix, the composition including the combination of a polishing materal, a soluble cerium salt and a soluble reactant which generates with the cerium salt a gelatinous or otherwise voluminous material.

A further object is to provide new and improved methods of preparing a polishing composition either as a slurry or a dry mix, the methods providing for controlled reaction between the constituents of the new compositions of the present invention.

Other objects not specifically set forth will become apparent from the following description of the present invention.

Generally, the polishing compositions of the present invention comprise a polishing material combined with a gelatinous constituent such as ceric hydroxide or a soluble cerium salt and a soluble reactant which generates with the cerium salt the gelatinous constituent. The composition may be prepared as a dry mix with the reactants capable of forming the gelatinous constituent being retained in non-reactive condition because of the dry nature of the mix. Upon hydration of the dry mix, the gelatinous constituent forming reactants combine to form the gelatinous ingredient which then combines with the polishing material in some suitable manner to improve the polishing speed of the resulting slurry or dispersion as well as improve the resistance to settling and caking thereof.

The gelatinous constituent of the polishing composition of the present invention is formed by the reaction of a suitable soluble cerium salt with a suitable soluble base or a suitable hydrolyzable salt which generates hydroxyl ions upon hydration of the reactants, or a salt giving anions in solution that will combine with cerium ions in solution to give a gelatinous material. Examples of soluble cerium salts are as follows:

Cerim ammonium nitrate
Ceric ammonium sulfate
Ceric sulfate
Cerous nitrate
Cerous sulfate

The foregoing does not constitute a complete list of suitable soluble cerium salts but is representative of the type of salt which is readily adapted for commercial use in the forming of a dry mix or slurried polishing composition.

A representative list of a suitable soluble compound having the appropriate anion for reaction with a soluble cerium salt to form the gelatinous constituent is as follows:

Sodium hydroxide
Potassium hydroxide
Ammonium hydroxide
Sodium metaborate
Sodium tetraborate
Sodium tetraborate pentahydrate
Sodium tetraborate decahydrate
Sodium carbonate
Trisodium phosphate

Other suitable reactants including the anhydrous forms of the salts listed as well as the potassium and ammonium derivatives of the various soluble bases and salts are equally suitable for reaction with the soluble cerium salts.

The gelatinous constituent formed upon reaction of

the soluble cerium salt with a suitable soluble base or salt is of a structure which is not well or readily defined. For purposes of describing this aspect of the present invention, it will be understood that the gelatinous constituent referred to as a gelatinous ceric hydroxide could possibly be more nearly considered a hydrous ceric oxide. Similarly, the gelatinous precipitates formed when solutions of hydrolyzable salts are added to solutions containing cerium ions may be hydrous cerium oxide or may be complex basic salts. The general classes of such compounds are known but extant knowledge is not sufficient to define clearly their complex structures.

In accordance with the teachings of the present invention, it has been found that the forming of the gelatinous ceric hydroxide in the presence of a suitable polishing material provides the polishing composition with an improved polishing speed rating, a much slower settling rate, and non-caking characteristics. In preparing the polishing composition, several different procedures may be followed with the composition being particularly adapted for formulation as a dry mix which is of particular commercial importance.

On a commercial basis, a chemical supplier formulates a polishing composition and ships the same to a glass product fabricator who then utilizes the composition in polishing operations. It can be readily appreciated that the formulation and shipping of a slurried polishing composition presents a number of difficulties particularly as the composition itself constitutes a very high percent of water and any tendencies of the slurry to settle out complicates the merchandising and subsequent use thereof. However, with the compositions of the present invention, the solid ingredients thereof may be mixed on a dry basis, stored and shipped in this condition with dispersion formation occurring at the location of glass polishing by the addition of adequate water accompanied by suitable mixing. The constituents of the dry mix constitute the polishing material, a dry non-reactive but water soluble cerium salt, and a dry non-reactive but soluble reactant which upon hydration of the mix generates with the cerium salt the gelatinous precipitate. The soluble bases or salts which are capable of generating with the cerium salts the gelatinous constituent and the cerium salts themselves preferably should be non-deliquescent for the formulation of a dry mix. However, deliquescent or otherwise reactive materials may be used if, for example, they are suitably encapsulated or otherwise treated to render them nonreactive during storage.

In the preparing of the polishing compositions in the form of a slurry or dispersion without utilizing dry mixing conditions, the polishing material may be mixed in water with a suitable soluble cerium salt followed by subsequent solution addition of the reactant capable of generating hydroxyl or other precipitate forming anions in the composition and thus forming therein the gelatinous precipitate. Conversely, the polishing material may be combined in a solution of the suitable cerium salt reactant followed by addition of the cerium salt to the mixture.

The following examples are illustrative of various polishing compositions prepared in accordance with the teachings of the present invention. It should be understood that these examples are not intended to be limiting to the scope of the invention as defined by the appended claims.

Example I

The following polishing composition was prepared in slurry form:

Constituents:	Parts by weight
Cerium oxide (polishing grade)	5.0
Water	100.0
Ceric ammonium nitrate	3.3
Sodium hydroxide	1.0
	109.3

A portion of the polishing grade cerium oxide used in this composition was separately tested for polishing speed determination by dispersing 5 parts of the oxide in 100 parts of water. The polishing speed was 10.0 based on the test procedure set forth above. The polishing composition resulting from the above-identified formulation was subjected to the same test with the result that a polishing speed value of 18.9 was attributable to the composition.

Example II

Constituents:	Parts by weight
Rare earth oxide (polishing grade)	8.0
Water	100.0
Cerous nitrate hexahydrate	2.5
Sodium carbonate	3.5
	114.0

The polishing grade rare earth oxide used contained about 40% cerium oxide, about 20% lanthanum oxide, and about 20% rare earth oxide mixture of principally neodymium and praseodymium oxide. 8 parts of this material were dispersed in 100 parts of water and a polishing speed of 9.6 was determined. The composition set forth above provided a polishing speed of 13.6.

Example III

Constituents:	Parts by weight
Rouge (polishing grade)	5.0
Water	100.0
Ceric ammonium nitrate	3.3
Sodium hydroxide	1.0
	109.3

A portion of the same batch of polishing grade rouge was dispersed in water on the basis of 5 parts rouge in 100 parts water. The polishing speed was 6.7. The polishing speed of the above-listed composition was 10.1.

The following examples deal with the formulation of a dry mix polishing composition.

Example IV

Constituents:	Parts by weight
Cerium oxide (polishing grade)	5.0
Ceric ammonium nitrate	3.0
Anhydrous sodium tetraborate	2.0
	10.0

A portion of the batch of polishing grade cerium oxide was dispersed in water on the basis of 5 parts cerium oxide for each 100 parts water and a polishing speed of 10.8 was determined. The above-identified dry mix was prepared by blending together the listed constituents by dry ball-milling the mixture for one hour. Following blending, the composition was dispersed in water and the polishing speed of the dispersion formed on the basis of 10 parts mix for each 100 parts water was 14.5.

Example V

Constituents:	Parts by weight
Rare earth oxide (polishing grade)	5.0
Ceric ammonium nitrate	3.3
Sodium tetraborate pentahydrate	3.0
	11.3

This dry mix was prepared in accordance with the procedure set forth in Example IV above and polishing speeds were determined in the same manner. The polishing speed of the rare earth oxide dispersed in water on the basis of 5 parts oxide to 100 parts of water was 8.9 and the polishing speed of the dispersed dry mix on the basis of 11.3 parts dry mix (containing 5 parts rare earth oxide) to 100 parts water was 16.2.

Example VI

Constituents:	Parts by weight
Zirconium oxide (polishing grade)	5.0
Ceric ammonium nitrate	3.3
Sodium tetraborate pentahydrate	3.0
	11.3

The procedure of Example IV was again followed and the polishing speed of the zirconium oxide dispersed in water on the basis of 5 parts zirconium oxide to 100 parts water was 6.6 with the polishing speed of the slurried dry mix on the basis of 13.3 parts dry mix (containing 5 parts zirconium oxide) to 100 parts water was 12.6.

Example VII

Constituents:	Parts by weight
Cerium oxide (polishing grade)	5.0
Ceric sulfate	1.0
Sodium metaborate	1.0
	7.0

The procedure of Example IV was followed and the polishing speed of the cerium oxide alone dispersed in water was 10.0 whereas the polishing speed of the dispersion formed on the basis of 7 parts dry mix (containing 5 parts cerium oxide) to 100 parts water was 15.0.

Example VIII

Constituents:	Parts by weight
Cerium oxide (polishing grade)	5.0
Ceric sulfate	3.0
Sodium metaborate	3.0
	11.0

The procedure of Example IV was followed with the cerium oxide dispersed by itself in water providing a polishing speed of 10.0. The dispersed and reacted dry mix provided a polishing speed of 16.2 on the basis of 11.0 parts mix (containing 5 parts cerium oxide) to 100 parts water.

The foregoing examples well illustrate the material improvement obtained in polishing speeds by use of the polishing compositions of the present invention. It has also been found that a materially slower settling rate is present with the dispersed polishing compositions of the present invention. By way of example, the settling rate can be 50 times slower than the settling rate of a polishing material such as cerium oxide dispersed solely in water. The settling that does occur over a protracted period of non-use of the polishing composition does not result in caking to an extent that redisposition of the slurry is difficult or excessively time consuming. In other words, the slurry will very readily redisperse to the extent that the solids therein have settled out even following protracted periods of non-use.

Examples I through III deal with the immediate formation of a polishing composition slurry and, as stated above, the order of addition of the various constituents may vary. In considering Example I, the cerium oxide and ceric ammonium nitrate are combined with the water and stirred resulting in the solvating of the ceric ammonium nitrate and the dispersing of the insoluble cerium oxide. The sodium hydroxide in solution form is then added to the dispersion and the reaction resulting in the formation of the gelatinous ceric hydroxide occurs immediately. The result is that a uniform dispersion or slurry of the combined cerium oxide and gelatinous ceric hydroxide is virtually instantaneously formed. The order of addition may be varied resulting in initial mixing of the cerium oxide with the sodium hydroxide in solution followed by the addition of the ceric ammonium nitrate with the same results.

For ophthalmic use of the polishing compositions of

the present invention, it has been found that a desirable ratio is 5 parts polishing material to 1 part equivalent cerium oxide in the soluble cerium salt. The broad preferred range for the various polishing compositions provides for the cerium salt being present in quantities sufficient to provide an equivalent cerium oxide to polishing material ratio within the range of from about 1 to 10 to 1 to 3 by weight. The pH of the polishing composition dispersion may vary considerably although it has been found preferable that the pH be about 5 when the dispersion is initially formed with ceric type salts, or about 8 when formed with cerous type salts. In the examples given, this can be controlled by the quantity of sodium hydroxide or other precipitant used.

Obviously certain modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A polishing composition, consisting of at least one polishing material selected from the group consisting of red rouge, zirconium oxide, cerium oxide and rare earth oxide combined with a gelatinous ceric hydroxide.

2. A polishing composition consisting essentially of a dispersion of at least one polishing material selected from the group consisting of red rouge, zirconium oxide, cerium oxide and rare earth oxide combined with a gelatinous ceric hydroxide.

3. A polishing composition consisting essentially of cerium oxide combined with a gelatinous ceric hydroxide.

4. A polishing composition consisting essentially of rare earth oxide combined with a gelatinous ceric hydroxide.

5. A polishing composition consisting essentially of a dry mix of at least one polishing material selected from the group consisting of red rouge, zirconium oxide, cerium oxide and rare earth oxide combined with a cerium salt selected from the group consisting of ceric ammonium sulfate, ceric ammonium nitrate, ceric sulfate, cerous nitrate and cerous sulfate and a reactant selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium metaborate, sodium tetraborate, sodium tetraborate pentahydrate, sodium tetraborate decahydrate, sodium carbonate and trisodium phosphate which generates with said cerium salt a gelatinous material upon hydration of said mix.

6. The method of preparing a polishing composition which exhibits improved polishing speed, said method comprising combining at least one polishing material selected from the group consisting of red rouge, zirconium oxide, cerium oxide and rare earth oxide with a cerium salt selected from the group consisting of ceric ammonium sulfate, ceric ammonium nitrate, ceric sulfate, cerous nitrate and cerous sulfate, and dispersing the resulting mixture in an aqueous solution of a reactant generating hydroxyl ions therein, said reactant being selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium metaborate, sodium tetraborate, sodium tetraborate pentahydrate, sodium tetraborate decahydrate, sodium carbonate and trisodium phosphate.

7. The method of preparing a polishing composition which exhibits improved polishing speed, said method comprising combining at least one polishing material selected from the group consisting of red rouge, zirconium oxide, cerium oxide and rare earth oxide with a cerium salt selected from the group consisting of ceric ammonium sulfate, ceric ammonium nitrate, ceric sulfate, cerous nitrate and cerous sulfate, and dispersing the resulting mixture in an aqueous solution of a reactant generating hydroxyl ions therein, said reactant being selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium metaborate, sodium tetraborate, sodium tetraborate pentahydrate, sodium tet-

raborate decahydrate, sodium carbonate and trisodium phosphate and said cerium salt being present in quantities sufficient to provide an equivalent cerium oxide to polishing material ratio within the range from about 1 to 10 to 1 to 3 by weight.

8. The method of claim 6 wherein the polishing material is first dispersed in said aqueous solution followed by the addition of the cerium salt thereto.

9. The method of preparing a polishing composition which exhibits improved polishing speed, said method comprising dry blending at least one polishing material selected from the group consisting of red rouge, zirconium oxide, cerium oxide and rare earth oxide, a dry cerium salt selected from the group consisting of ceric ammonium sulfate, ceric ammonium nitrate, ceric sulfate, cerous nitrate and cerous sulfate and a dry material which is capable of generating hydroxyl ions upon hydration, and subsequently forming a gelatinous dispersion of the dry blend by adding water thereto, said dry material being selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium metaborate, sodium tetraborate, sodium tetraborate pentahydrate, sodium tetraborate decahydrate, sodium carbonate and trisodium phosphate.

10. The method of preparing a polishing composition which exhibits improved polishing speed, said method comprising dry blending at least one polishing material selected from the group consisting of red rouge, zirconium oxide, cerium oxide and rare earth oxide, a dry cerium salt selected from the group consisting of ceric ammonium sulfate, ceric ammonium nitrate, ceric sulfate, cerous nitrate and cerous sulfate and a dry material which is capable of generating hydroxyl ions upon hydration, and subsequently forming a gelatinous dispersion of the dry blend by adding water thereto, said dry material being selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium metaborate, sodium tetraborate, sodium tetraborate pentahydrate, sodium tetraborate decahydrate, sodium carbonate and trisodium phosphate and said cerium salt being present in quantities sufficient to provide an equivalent cerium oxide to polishing material ratio within the range of from about 1 to 10 to 1 to 3 by weight.

11. A glass polishing composition consisting essentially of water, cerium oxide and chemically active cerium hydroxide.

12. A glass polishing composition consisting essentially of water, zirconium oxide, and chemically active cerium hydroxide.

13. A polishing composition consisting essentially of zirconium oxide combined with a gelatinous ceric hydroxide.

14. A polishing composition consisting essentially of iron oxide combined with a gelatinous ceric hydroxide.

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