Original Paper

Properties of polishing media for precision optics

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The first theory concerning the polishing of glass, which viewed polishing as an extension of the grinding process with finer abrasives, and the flow theory of Beilby, both stipulate purely hypothetically that the polishing grains should have a very high hardness. This hypothesis of high hardness of the polishing grains was so strongly supported by Smekal and Brüche in the 40's and 50's and by other scientists in the following years that it became dogma, i.e., a claim without proof, and has remained virtually universally accepted to this day. The results of the investigations of the present author have shown, however, that first, extra lattice defects in the crystalline oxides used as polishing agents are the primary characteristics that are responsible for the gripping of the grains during polishing and second, the hardness of the grains of the polishing agent must be lower than that of the material which is being polished. By and large these results have been ignored in the literature, because they are in opposition to the dogma that the polishing agent must have a high hardness. Clear proof is presented in this paper that disproves the generally accepted hypothesis that polishing can be done with very fine grinding powder, and that the polishing agent must be harder than the glass which is to be polished. The properties of polishing agents for use in polishing for precision optics will be described on the basis of the theory of polishing agents containing lattice defects.

Eigenschaften von Poliermitteln für die Präzisionsoptik

Sowohl die erste Poliertheorie von Glas als Fortsetzung des Schleifprozesses mit feineren Schleifmitteln und die Fließtheorie von Beilby schreiben den Polierkörnern rein hypothetisch sehr hohe Härten vor. Die Hypothese von der hohen Härte der Polierkörner wurde durch die bekannten Wissenschaftler Smekal und Brüche in den 40er und 50er Jahren so stark unterstützt, daß sie zum Dogma, d.h. zur Behauptung ohne Beweis, wurde und dadurch noch bis zum heutigen Tage weltweit anerkannt wird. Die Ergebnisse der eigenen Untersuchungen in 18 Veröffentlichungen, die die jeweils zusätzlich eingebauten starken Gitterstörungen in die kristallinen Poliermitteloxide als Haupteigenschaften für deren Griffigkeit beim Polieren verantwortlich machen, blieben in der Fachliteratur weitgehend unberücksichtigt, da sie dem Dogma von der hohen Härte der Poliermittel widersprachen. Mit eindeutigen Beweisen wird die allgemein übernommene Hypothese widerlegt, daß man mit jedem Schleifmittel feinster Körnung auch polieren könnte und daß das Poliermittel härter sein muß als das zu polierende Glas. Die Eigenschaften der Poliermittel werden anhand der Gitterstörtheorie der Poliermittel für den Einsatz beim formbildenden Poliervorgang beschrieben.

1. Introduction and formulation of the problem

In [1] Karow laments that the properties of polishing agents are practically unknown. For example, the 48 CeO_2 polishing agents on the American market are subdivided into only three quality groups, which, except for characterizations of "highest quality" to "economical", are put into the three groups according to their particle sizes: a) 0.5 to 1.0 µm, b) 1 to 3 µm, and c) 1 to 10 µm. The American division of the CeO_2 polishing agents into three quality groups has also been accepted by the Treibacher Chemische Werke in Austria in their new catalog of CeO_2 polishing media. Only the CeO_2 content and the particle size are listed.

The lack of knowledge about the properties of polishing media can be explained by the wide acceptance of the hypothesis of needing a polishing agent with a high hardness. This hypothesis has its roots in the earlier belief that polishing is an extension of grinding, but with finer abrasives. Later, the hypothesis was strengthened by the flow theory of Beilby [2], the theory of Klemm and Smekal [3 and 4], and especially the opinion of Smekal [5], that the polishing agent always has to be harder than the glass which is being polished, and that polishing can be done with any grinding powder as long as the particle size is small enough. In large part because of these publications, some German-English dictionaries still translate the words "schleifen" = grinding or polishing and "Schleifmittel" = grinding or polishing agent. Also, the hypothesis of the high hardness of the polishing agent allows no properties other than the particle size to be used in characterizing gripping for use in polishing, since no method exists for determining the hardness of powders.

Actually, the hypothesis of the high hardness of the polishing agent only has validity for crystals that have a Mohs hardness of 8 to 10, e.g., the gemstones topaz, sapphire, ruby, and diamond, since these can only be

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polished with diamond powder. Diamond itself is polished by using a still harder type of diamond. This is not true of glass, however, and this can be proven. According to the theory described earlier, polishing of glass involves a smoothing, quasiplastic material displacement parallel to the glass surface, whereby removal of glass only plays a minor role. However, this is not in accordance with the fact that glass removal actually is the major process during polishing of glass. For example, removal rates as high as 20 µm/min have been measured during polishing of eyeglass lenses using CeO_2.

In his paper on then-new theories about polishing optical glasses [6], Minář confirms that the hypothesis of the high hardness of the polishing agent is the main feature of the theory of Klemm and Smekal. The present author, howover, in his first publications concerning polishing of glass [7 and 8], which were based on the lattice-defect theory of the oxide polishing agents, was of the opposite opinion, namely that the polishing agent must always be softer than the glass being polished. These publications formed the basis of an extensive discussion that took place during the meeting of Technical Committee I (FA I) of the Deutsche Glastechnische Gesellschaft (DGG) on 2 and 3 November 1956 in Würzburg. The published report of this meeting contains only the following summary of this discussion [9]: "The difference in the opinions of Kaller and Smekal is that Kaller investigated the technical polishing process whereas Smekal carried out his work purely theoretically from the point of view of a physicist". However, Smekal emphasized in the discussion that, although the chemistry during polishing described by Kaller surely plays a role, i.e., processes caused by lattice defects in the oxides being used as polishing agents, this was an unproved opinion for two reasons. The first reason given by Smekal was the fact that the very fine particles created by breakup of the polishing grains could not be verified using the electron microscope. The second reason cited was that such an extensive fragmentation of the small polishing grains was not possible. Based on earlier experimental results [10], Smekal believed that brittle materials could lose their brittleness when the fragments became smaller than 1 µm, so that there would be a limit to the smallest size particle that could be produced by crushing. Other references address this point [11 to 13]. The present author was not able to answer these objections in 1956, because too few experiments had been performed. Both of these objections will be addressed later in this paper.

Brüche [14] agreed with Smekal in rejecting the lattice-defect theory of the polishing agents in his summary of the present author's publication in which he wrote: "This interesting theory of polishing, which is very definitely and extensively presented, has, unfortunately, no very convincing experimental basis".

The hypothesis of the polishing agent needing a high hardness was supported by many authors in the following years. These include Izumitani and Sakata (Japan), Wawrziniak and Dunken (Jena), Brown, Cook, and Fuchs (Lawrence Livermore Laboratory, USA). These references were cited and discussed in a previous paper [15], so they will not be repeated here. According to Cook, the Lawrence Livermore authors support the widely accepted mechanochemical polishing mechanism [15]. This is described as a two-phase mechanism. In the first phase, interaction with water causes a silica-gel layer to form on the glass surface. In the second phase, this gel layer is mechanically scraped off by the polishing agent. Clearly implied in this, even though not stated directly, is that the polishing agent must be harder than the silica-gel layer. The topic of the "hardness" of the polishing grains will he discussed later.

Unfortunately, this introduction of the term "mechanochemical" in the American literature in connection with the role of chemistry during polishing of glass has allowed a regrettable nomenclature error to creep into the literature on polishing. The term "mechanochemistry" was coined by Ostwald [16] for a branch of physical chemistry (see e.g. Peter [17, p. 81]), and Ostwald placed this branch at the same level as thermochemistry, electrochemistry, magnetochemistry, and photochemistry. "Mechanochemistry" was not a subject of much research initially, but Peter [17] had many publications and colloquies in this area in the 50's. Thiessen [18] and his co-workers [19] elucidated the term "tribochemistry", which appeared in print for the first time in 1963 [18 and 19]. This is a subgroup of "mechanochemistry" and confirms the complete acceptance of "mechanochemistry" as a branch of physical chemistry.

The expression "mechanochemistry" has become so well established in English usage in connection with polishing, despite its being in conflict with recognized nomenclature, that it can no longer be changed. One has to keep this in mind when encountering this expression in English-language literature. Because the present author uses the expression "tribochemistry" as the fundamental concept for his polishing theory, it is necessary to provide a list of definitions of terms as follows:

- Tribology [20]: The science of friction and wear of parts moving against one another.
- Tribochemistry [19, p. 113 and 114]: A branch of mechanochemistry. Tribochemistry is a branch of chemistry which is concerned with chemical and physical-chemical changes in solids as a result of the application of mechanical energy.
- Mechanochemistry [19, p. 113 and 114]: The superordinate branch of tribochemistry. Mechanochemistry is a branch of chemistry which is concerned with chemical and physical-chemical changes of substances of all states (i.e., solids, liquids, and gases) as a result of the application of mechanical energy.

Keeping these definitions in mind, the polishing process can be called a tribochemical process, and it can be explained very well on the basis of the assumption that the most important property of gripping polishing agents is the presence in these oxides of a large number

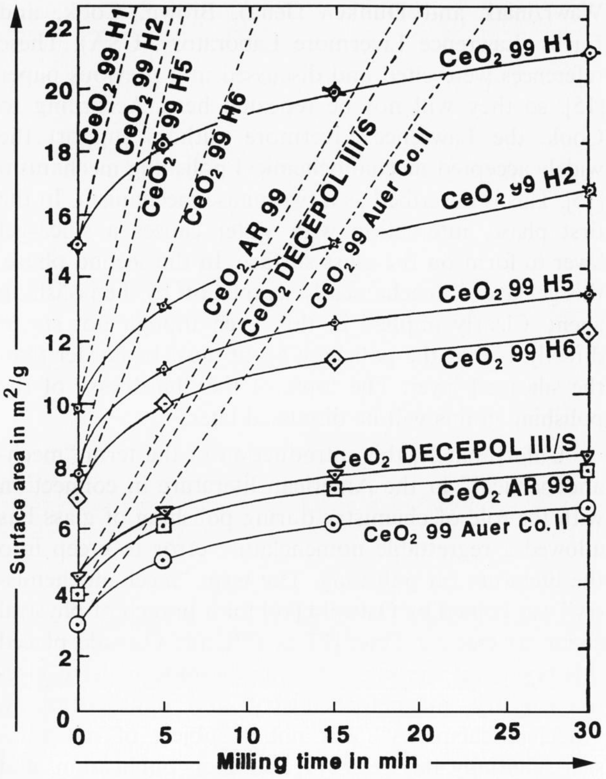

Figure 1. Increase in the surface areas of various CeO_2 samples in dependence on milling time in a vibratory mill with 5-mm-diameter steel balls.

of lattice defects, which are produced during their manufacture. The tribochemical polishing process has the following three steps:

a) The intimate contact between polishing grains and the glass surface, together with the associated mechanical friction or shear forces, create strong lattice deformation in the surface layers of these grains and a certain amount of partial removal of these surface layers due to the rubbing action between grains and glass surface.

b) Removal of surface layers of polishing grains exposes the ionic vacancies in the lattice which are also present, and which, as they are exposed, enter into "in statu nascendi" solidstate reactions with components in the glass surface.

c) The continuing motion of the polishing wheel then rips out nanoscale pieces of the glass surface which bonded with exposed, active surfaces of polishing grains in step b), thus, producing a continuous removal of the glass surface during polishing.

Japanese authors [21 to 23] drew some interesting conclusions regarding high hardness values of polishing grains from their ellipsometry investigations of polished layers on quartz glass surfaces. Surprisingly, the index of refraction of these layers is slightly higher than that of the bulk, whereas with normal silicate glasses, the polished layers have a lower index of refraction than that of the base glass. The explanation that was offered for the higher index of refraction of the polished layer was that the silica-gel layer was densified by the high local pressure of the hard grains of the polishing agent. In this way, the index of refraction of the polished layer was raised slightly from 1.461 to 1.467 by increasing the polishing load from 4 to 40 kPa in comparison to a refraction index of 1.459 for the quartz glass. In reality, however, this slight increase in index of refraction can be explained by the incorporation of very small particles during polishing with CeO_2 polishing agents, particles as small as the size of cerium ions, which are removed from CeO_2 grains by abrade.

Polishing of glasses with a slightly radioactive ThO_2 polishing medium provided evidence that rubbing of polishing grains produces particles as small as ions which are then adsorbed by the polished layer. Although ThO_2 is completely insoluble in water, the surfaces of four different optical glasses, after polishing on a polishing felt with ThO_2 suspended in water alone or in a 5 % $ThCl_4$ solution, showed the same weak radioactivity, since Th^{4+} ions were adsorbed in both cases [24].

It will be recalled that Smekal had two objections that could not be answered at the time; namely, first, that the very small particles produced by rub down of the polishing grains could not be seen in the electron microscope and second, that grains below a certain limiting size could not be broken further into still smaller pieces. However, the present state of knowledge provides answers to these two objections.

To the first, as early as 1959, Rebentisch and Dinkelacker [25] were able to measure an extremely small attrition of polishing grains as a result of polishing. They established this by measuring 3000 to 4000 polishing grains in an electron microscope before and after a simulated polishing lasting 5 h. They found that polishing grains that were in the range 30 to 300 nm were 20 nm smaller on average (about 7.4 %) after 5 h of rubbing in the simulated polishing. Any particles that were produced were so small that colloidal effects prevented their being seen.

Other experiments were undertaken in order to answer the second objection. The reason given earlier for the size limit for fracturing particles was that particles smaller than 1 µm behave plastically [10 to 13]. The intent of these new investigations was to see if this assumption holds for polishing grains that contain a significant number of lattice defects. Accordingly, many different Fe_2O_3 and CeO_2 polishing agents were milled in high vacuum in a small vibratory mill. BET measurements before and after milling confirmed an increase in the surface areas of the polishing agents. The Fe_2O_3 samples were milled for 50 h using 10-mm glass beads; the CeO_2 samples were milled for only 5, 15, and 30 min using 5-mm steel balls. The results for the eight Fe_2O_3 samples are presented in [24]. The results of the milling experiments on the CeO_2 samples are presented in the curves shown in figure 1. It is seen that the attrition process is about the same for all specimens, independent of the starting size of the polishing grains, and that all curves approach a limiting value for the size reduction, as indicated by a limit to the increase in surface area. This limit to size reduction in the vibratory mill is caused by the fact that the reduced particles remain in the mill and, because of their very active fresh fracture surfaces, increasingly coat the surfaces of the milling balls and of the mill interior, thereby causing a reduction in the milling surfaces and the consequent cessation of further size reduction. If the milled material, with its final particle size, were to be placed in a fresh mill with fresh milling balls, the attrition process would begin anew, and with about the same rate as the first time.

Therefore, it can be stated that the tendency of the attrition of all polishing agents to achieve some limiting value, as in the curves shown in figure 1, is only true for a chosen set of conditions. In reality, attrition would follow without limit the dashed lines in figure 1, if the milling balls and mill container were changed frequently.

The size reduction of two Fe_2O_3 specimens will be covered in detail in section 2.2. It can be mentioned here, however, that these two materials, one obtained from γ-FeO(OH) and one from α-FeO(OH), have, surprisingly, completely opposite behaviors in milling experiments, even though they have similar particle sizes (12.1 nm or 106.0 m^2/g surface area for γ-Fe_2O_3; 11.5 nm or 99.7 m^2/g surface area for α-Fe_2O_3). The γ-Fe_2O_3 specimen, which has very many lattice defects, is exceptionally easy to reduce in size by milling, whereas the α-Fe_2O_3 sample, which has none lattice defects, shows no change in particle size after 50 h of milling.

Thus, both objections of Smekal to the lattice-defect theory of polishing agents have been refuted by experimental evidence that did not exist at the time. The hypothesis represented by others that the polishing agent must be harder than the material being polished or that polishing can be done with any abrasive having extremely fine particle sizes will be refuted by similar experimental evidence later in this article.

2. Experiments on the properties of polishing agents

2.1 Internal structure of crystalline oxides used as polishing agents

The present author's own findings indicate that the fundamental characteristics of the internal structure of polishing oxides include the primary crystallite size, the number of primary crystallites which have crystallized together to form a grain, the crystal system of the primary crystallites, and the lattice defects contained in the primary crystallites. There are two types of polishing oxides based on the internal structure of the grains. First, individual particles are grains consisting only of a certain number of primary crystallites that have approximately the same size, e.g., 40 to 60 nm, as in CeO_2 99 H1 (table 1) or 185 to 205 nm, as in CeO_2 99 Auer, Berlin [26]. Second, individual particles may consist of many grains of the first type that are weakly or strongly sintered together. The term grain itself is used here in the sense of a particle of a polishing agent that was produced during the manufacturing process and not during a subsequent milling operation.

The first type of polishing agent, i.e., the one which consists of grains composed of primary crystallites, is formed from hydroxides of Fe^{2+} ions or Ce^{3+} or Ce^{4+} ions, while the second type is formed by calcining organic iron(II) of cerium(III) compounds, such as iron(II) or cerium(III) oxalates. In the latter two cases, Fe_2O_3 or CeO_2 products are formed, which have the shape and size of the beginning oxalates, i.e., about 10 to 20 µm, but which have pores resulting from weight losses of 56 % in the first case and 51 % in the second case. Electron microscope images [25, figure 5] show that the resulting particles consist of individual grains which have sintered together. These must be broken up through milling prior to their being used for polishing. These milled particles are not individual grains, however, but rather are particles of random size, e.g., from less than 1 to about 10 µm, according to milling time. The size of the primary crystallites depends on the firing schedule (temperature and time) used to make the polishing agent. More will be said about this in sections 2.2 and 2.4. The best polishing agents have primary crystallites which belong to the cubic crystal system, as reported earlier in [15].

One of the most important characteristics of the internal structure of polishing grains is the number of additional lattice defects produced during manufacture which are present in the primary crystallites. The lattice disorders that are always present to a greater or lesser extent in crystals are very minor in comparison to the additional lattice defects produced in large numbers during manufacture, so that the intrinsic lattice disorders have no appreciable influence on the gripping of these oxides during polishing. For this reason, in the rest of the article, the expression "lattice defects" will be used instead of "additional lattice defects".

Lattice defects of the primary crystallites of polishing agents, which have an influence on the gripping during polishing, can be created in various ways. First, there can be a transition from one form of the oxide into another, e.g., through a change in valence of the metal ion in the solid state. The strongest lattice defects with the highest bonding energy are produced by cation holes, i.e., vacancies as described by Kossel [27] and Stranski [28]. The value of the bonding energies of the cation holes increases with increasing valence of the oxide cation. The second way in which lattice defects can be produced is through the incorporation of foreign metal ions or molecules. This form of lattice defect is stronger, the larger the difference between host and foreign atoms or ions with respect to volume, charge, and electron configuration [29]. These defects also lead to an opening-

Table 1. Several examples of the inner structure of polishing agents based on Fe_2O_3 and CeO_2

sample no.	polishing agent	firing temperature in °C	density in g/cm^3	surface area by BET in m^2/g	primary crystallite size in nm	size of polishing grains in nm	ratio of size of polishing grain to primary crystallite size	lattice defects
1	γ-Fe_2O_3 after [31]	225	4.67	106.0	4.0	12.1	3.025	very large
2	α-Fe_2O_3 after [32]	300	5.23	99.7	7.0 to 12.4	11.5	1.185	none
3	CeO_2 99 Vitrox C [33]	1000 to 1090	6.5	8.05	40 to 47	115.1	2.646	small
4	CeO_2 209/820/3	820	7.0	6.57	51 to 59	131.0	2.382	large
5	CeO_2 99 H1	820	7.0	15.0	40 to 60	57.4	1.148	very large

up of the lattice. Examples of improved polishing action through incorporation of foreign components in the oxide lattice are Ni^{2+} ions added to the Fe_2O_3 lattice, or small amounts of MgO or CeO_2 in the ZrO_2 lattice (see the example at the end of section 2.2), whereby monoclinic ZrO_2 is transformed into a cubic modification having the fluorite structure [15]. Thirdly, lattice defects can be createt during the process of producing the polishing agent itself. The polishing agent has to be produced at a very high temperature during a very short period of time and then suddenly quenched to a lower temperature (see the production of Zeiss's polishing Rouges no. 32 and no. 19 described in section 2.2). As a fourth way, lattice defect can be created through the freezing-in of thermal vibration [30] after the polishing agent which had been kept at a very high temperature for a much longer period of time is suddenly cooled down to a lower temperature.

Table 1 shows several examples of the internal structures of Fe_2O_3 and CeO_2 polishing agents. The primary crystallites in Fe_2O_3 polishing agents are considerably smaller than those in CeO_2 polishing agents. The sizes increase with increasing temperature, while the extent of lattice defects decreases. The control of the polishing properties of polishing agents through control of the primary crystallite sizes will be treated in section 2.4.

2.2 Properties of iron oxide polishing agents

The relationship between the properties of the polishing agents and their polishing characteristics were first investigated in iron oxides. For this purpose, various Fe_2O_3 products were produced using information in the literature, and their polishing effectiveness was studied. A great help in this was the fact that, in the 30's, in connection with the development of iron oxide magnetic recording tape, a great many theoretical projects were carried out concerning the manufacture of iron oxides using widely differing methods, and that exact determinations of the dependence of the properties of these oxides on the method of manufacture were performed. When the polishing effectiveness of these model iron oxides was investigated, the surprising result was that iron oxides that exhibited strong lattice defects, according to literature reports, were very effective in polishing, while those that had no or only slight structural defects were completely ineffective as polishing agents. Table 2 shows the steps in manufacturing several model iron oxide polishing agents. One must also take into account that lattice defects reduce the mechanical strength of the particles by up to several orders of magnitude lower than the strength of the same specimens without lattice defects [35].

The γ-Fe_2O_3 sample no. 1, which was made using γ-FeO(OH), serves as an important example of an oxide with a very high concentration of lattice defects. When the relatively low value of 4.9 kN/m^2 = 4.9 kPa for the polishing load at a peripheral speed of 30 cm/s in average is exceeded, so many lattice defects are released by the continual rubbing of the highly disordered polishing grains that the concentration of those lattice defects which bond immediately with the glass surface becomes high enough to give the glass surface a brown color. In fact, so much γ-Fe_2O_3 bonds to the surface that further removal of glass ceases. A milling experiment of the γ-Fe_2O_3 sample no. 1 conducted in a small vibratory mill in vacuum provides further proof that the rubbing of the polishing grains of this sample is especially high.

The BET surface area of this sample before milling was 106 m^2/g. After 50 h of milling, the surface area decreased about 25 % rather than increased, and was then only 79.5 m^2/g. This material has to be heated above 550 °C for the lattice defects to decrease sufficiently so that good polishing is achieved at a value of 19.6 kN/m^2 = 19.6 kPa for the polishing load at a peripheral speed of 70 cm/s in average.

The α-Fe_2O_3 sample no. 2, which was made from Fe^{3+} ions using α-FeO(OH) [32], has no lattice defects

Table 2. Steps in manufacturing several model iron oxide polishing agents

1. γ-Fe_2O_3 according to [31]	$Fe^{2+} \xrightarrow{\text{Urotropine}^{1)}} Fe(OH)_2 \xrightarrow[NaNO_2]{O_2} \gamma\text{-}FeOOH \xrightarrow{225\,°C} \gamma\text{-}Fe_2O_3$
2. α-Fe_2O_3 according to [32]	$Fe^{3+} \xrightarrow{3\,NH_4OH} Fe(OH)_3 \xrightarrow[H_2O;\ 100\,°C]{KOH} \alpha\text{-}FeOOH \xrightarrow{300\,°C} \alpha\text{-}Fe_2O_3$
3. γ-Fe_2O_3 according to [34]	$Fe^{2+} \xrightarrow{2\,NH_4OH} Fe(OH)_2 \xrightarrow[NH_4NO_3]{O_2} Fe_3O_4 \xrightarrow{300\,°C} \gamma\text{-}Fe_2O_3$
4. γ-Fe_2O_3 from Fe(II) formate	$6\,Fe(CHO_2)_2 \cdot H_2O \xrightarrow{250\,°C} 6\,FeO + 12\,CO + 18\,H_2O$ $6\,FeO \xrightarrow[200\,°C]{O_2} 2\,Fe_3O_4 \xrightarrow[500\,°C]{{}^1/_2\,O_2} 3\ \gamma\text{-}Fe_2O_3$
5. Zeiss polishing Rouge no. 32	Fe(II)oxalate + Fe(II)sulfate + + potassium chlorate + + wheat starch $\xrightarrow[\text{ca. }1300\,°C]{\text{small explosion}}$ raw mixture of polishing Rouge no. 32
6. Zeiss polishing Rouge no. 19	Fe(II)sulfate + potassium chlorate (large excess) + + wheat starch $\xrightarrow[\text{ca. }1000\,°C]{\text{small explosion}}$ raw mixture of polishing Rouge no. 19 in the melt of potassium chlorate

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1) Hexamethylentetramin

and no polishing effect [24], even after stepwise heating between 300 and 700 °C. A control milling experiment on this material in a small vibratory mill, analogous to that carried out for sample no. 1, produced no change in the BET surface area of 99.7 m^2/g after 50 h of milling. This result provides important confirmation that only oxide polishing agents that have additional lattice defects experience a positive influence on the polishing process through partial rub off removal of minute particles, while crystalline oxides that have no extra lattice defects do not experience this rub off removal during polishing and, thereby, also have no polishing effect.

In the Fe_2O_3 samples no. 3 and 4, γ-Fe_2O_3 was formed from magnetite (Fe_3O_4). The transition of the structure from magnetite to γ-Fe_2O_3 is very interesting. Very exact investigations were performed in the 30's and were described earlier in [8]. In summary, it can be stated that nine γ-Fe_2O_3 unit cells are formed from eight magnetite unit cells, whereby one-ninth of the iron ion positions in the nine γ-Fe_2O_3 unit cells are not occupied. Since such a high percentage of iron ion positions in γ-Fe_2O_3 is not occupied, it follows that this oxide has a high amount of lattice defects in the form of cation vacancies.

Zeiss polishing Rouges no. 32 and 19 (samples no. 5 and 6 in table 2), which have been manufactured and used in Jena since around 1912, are further examples that lattice defects in oxide polishing agents are responsible for their good polishing effectiveness. Polishing agents no. 19 and 32 were made from the mixtures presented in table 2. To do this, small amounts of the mixtures (200 to 300 g) were brought to explosion by pouring them from hand shovels into a 100-l sheet-iron container onto a burning cloth that had been soaked in alcohol. After each such small explosion, a small amount of the exploded mixture flew into the air, but most remained in the container.

The main component of polishing Rouge no. 19 is a basic iron oxide sulfate with the chemical formula of jarocite, $K(Fe^{3+}O)_3(SO_4)_2$ [15], which crystallizes in a layer structure, and which takes the form of very thin platelets. This polishing rouge is especially useful for the final polishing of glass surfaces where there is a premium placed on cleanliness, dimensional tolerances, and edge sharpness. The jarocite produced by explosion from the divalent iron salt (polishing Rouge no. 19) has a high amount of lattice defects, whereby synthetic jarocite produced more easily from trivalent iron ions has no polishing effect, since there was no change in valence state of the iron ions in the solid state and, therefore, no corresponding lattice defects. The same is true for the natural mineral jarocite (yellow ironstone).

The high polishing effect of the Zeiss "explosion" polishing agents no. 19 and 32 is caused by the short time at high temperature (table 2), which causes the formation of very large primary crystallites of the oxide, and the sudden, very severe quenching, which leads to many frozen-in lattice defects. In addition, the explosion which produces the polishing agent also distributes the oxide conglomerate formed from the iron(II) oxalate [25, figure 5] among the individual polishing grains.

Evidence for the good polishing effectiveness of a metal oxide polishing agent being caused by the presence of lattice defects, especially in the form of cation vacancies, is provided not only by the iron oxides, but also by all metal oxide polishing agents. Even metal oxides whose metal ions exist in only one valence state, e.g., those of aluminum or zirconium, which eliminates the

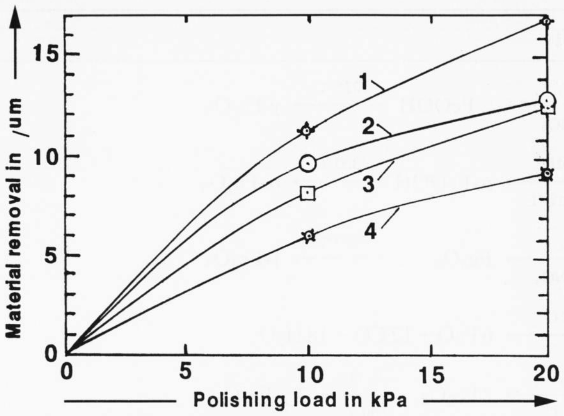

Figure 2. Polishing of quartz and quartz glass on polishing pitch for 4 h. Curve 1: quartz glass polished with CeO_2, Auer Co. II; curve 2: quartz glass polished with Red 168A (γ-Fe_2O_3); curve 3: quartz polished with CeO_2, Auer Co. II; curve 4: quartz polished with Red 168A (γ-Fe_2O_3).

possibility of a change in valency, can show good polishing effectiveness if lattice defects can be produced in some other way. For example, small amounts of MgO or CeO_2 added to ZrO_2 cause a change from the monoclinic form to a modified cubic form, which leads to a doubling of the polishing effectiveness on glass compared to the monoclinic form of ZrO_2 [36]. Similarly, the transformation of aluminum hydroxide into γ-Al_2O_3 leads to 2/3 of the metal ion positions in the unit cell of γ-Al_2O_3 being vacant [37].

2.3 Presentation of arguments why a gripping polishing agent must always be softer than the material being polished

It could be shown that γ-Fe_2O_3 (no. 3 or 4 in table 2) is very appropriate for providing the proof of the above statement. Recall that this material is obtained through oxidation of Fe_3O_4 at 300 °C, followed by a short heating at 450 °C, and that it has a large number of lattice defects owing to one-ninth of the iron ion positions being vacant. This γ-Fe_2O_3 has no problems removing material at a constan rate from the hardest glass, vitreous quartz, and also from crystalline quartz (with a Mohs hardness of 7) during polishing times of 4 h on an HM4 optical polishing machine at 9.8 and 19.6 kN/m^2 = 9.8 and 19.6 kPa, respectively (figure 2).

On the basis of the very low processing temperature of 450 °C and the presence of a large number of lattice defects, it can be estimated that the γ-Fe_2O_3 material used in these tests has a Mohs hardness of about 4 to 4.5. (The material designated in figure 2 as Red 168A is the γ-Fe_2O_3 described here.) If Fe_2O_3 were to be heated to a temperature of over 1400 °C, in the best case it would only be able to reach the Mohs hardness of hematite, i.e., 6.5, which is hard enough to scratch any optical glass, but not crystalline quartz, since the mineral hematite itself cannot scratch quartz. In contrast, as shown by the results presented in figure 2, the soft γ-Fe_2O_3, which is at least two peaces softer than quartz on the Mohs scale, can remove material tribochemically at a constant velocity from a quartz surface during polishing. Tribochemical reactions do not obey the laws of thermodynamics, but instead proceed according to their own set of complicated tribochemical laws, as pointed out in [19].

Besides the proof presented here, it is known that other hard materials can be polished tribochemically by very much softer materials; for example, various steels can be polished with Vienna lime, which has a Mohs hardness of 3. Feuerbach's patent [38] describes a process for polishing surfaces of hard materials using a soft graphite with Mohs hardness of 1. The materials listed in the patent include steels, hard metals, and coatings of hard compounds, especially nitrides, carbides, silicides, and borides. Pure graphite which has been milled in ball mills has minimal polishing action. On the other hand, coarse graphite powder obtained by drilling or by turning in a lathe is very effective in polishing, because of a tribochemical reaction.

All of this evidence clearly refutes the hypothesis that the polishing agent must be harder than the material being polished.

2.4 Properties of CeO_2 polishing agents

The cerium oxide polishing agent that was first put into use by Zeiss in Jena in 1933 came from the Auer Company in Berlin, which had pure cerium salts left over from the production of gas incandescent mantles and sought new applications for these byproducts. The 99 % CeO_2 was first used in small quantities in addition to polishing rouge, but today it has driven polishing rouge nearly completely out of the optical workshops, since it is considerably more effective than rouge. The high efficiency in comparison to rouge is based on the fact that the cerium ion in the CeO_2 lattice has a valence of +4, while the iron ion in the Fe_2O_3 lattice has a valence of +3, which means that the lattice defects in the CeO_2 polishing agent have a higher binding energy [27 and 28]. CeO_2 crystallizes in the crystal class with the highest symmetry, which brings distinct advantages because of a better heteropolarity than iron oxide, which is rhombohedral [39]. The good gripping of CeO_2 during polishing also comes from the lattice defects built into its crystal lattice during manufacturing.

Already described in section 2.1 was the external form of the CeO_2 polishing agent, which is made by precipitation with ammonium or calcining of cerium(III) oxalate or formate. It can be added that the CeO_2 polishing agent which is made by calcining of organic cerium(III) compounds and which does not exist as individual grains, is not nearly as appropriate for polishing of precision optics as CeO_2 obtained through hydroxide precipitation. The further thermal treatment of the oxide/hydroxide preliminary products must follow certain rules, which will be explained in section 2.5.

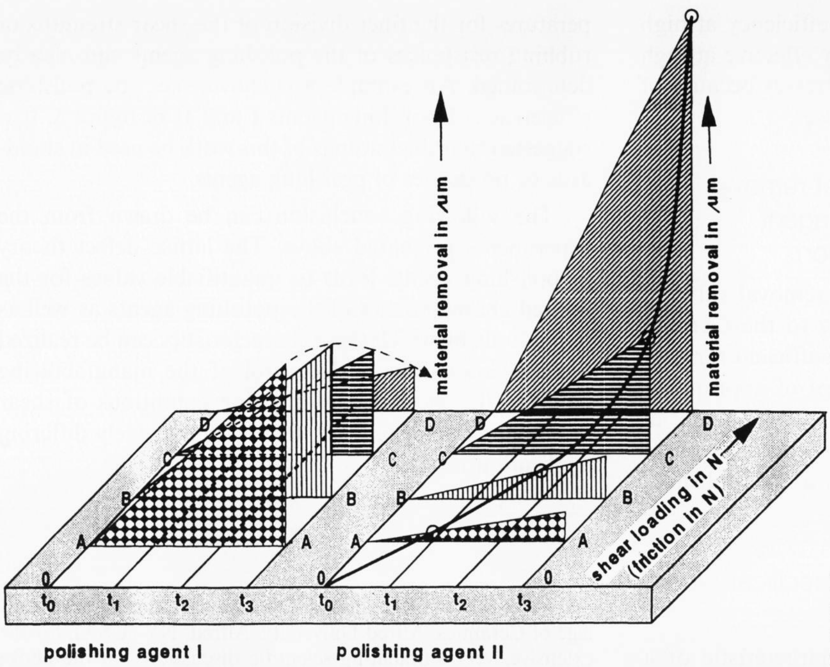

Figure 3. Schematic diagram showing the polishing effectiveness of polishing agents I and II as glass material removal as a function of polishing time and shear loading.

2.5 CeO_2 polishing agents with optimum shear strength or rubbing resistance (or rubbing hardness) for particular polishing parameters

To work an optic in dependence on the degree of precision, the polishing parameters of the polishing machine must be matched in very wide ranges with the shear strengths or rubbing resistances of the polishing agents. However, since the rubbing resistance of a particular polishing agent can only be adjusted in a narrow range, because of the built-in extra lattice defects, it is necessary to have several polishing agents with a range of rubbing resistances available in order to be able to use a wide adjustment range for the parameters of the polishing machine.

Control of the manufacturing of CeO_2 polishing agents with precisely adjusted values of rubbing resistance can be accomplished through increasing the size of the primary crystallites as well as through a decrease in the lattice defects in dependence on the thermal treatment of the polishing precursors. In order to do this, one must know the entire curve for the increase in the size of the primary crystallites as well as for the decrease of the lattice defects, as shown by Fricke [15, figure 1], for the temperature region from about 400 to 1400 °C. Fine control in producing different ranges of rubbing resistance of the polishing agents is done in the steeply increasing part of the crystallite growth curve by heating the precursor materials until the desired average primary crystallite sizes of, for example, 50, 120, and 200 nm are achieved. The corresponding heating times must be determined empirically through polishing experiments.

The oxide polishing agents produced in the initial stage of the temperature region corresponding to the steep part of the crystallite growth curve have the strongest lattice defects, but this means they also have the lowest rubbing resistance or rubbing hardness, i.e., they are very soft. Therefore, they can only be used with slowly running machines and at low polishing pressures.

Increasing the production temperature in order to produce primary crystallites of selected sizes diminishes the lattice defects, but raises the abrasion resistance, so that a more efficient removal of material is achieved by being able to run the polishing wheels at higher rotation speeds at higher pressures.

A high degree of uniformity for the individual grains of the polishing agent is also important for the performance of a polishing agent in any particular region of rubbing resistance. The finer the grains, e.g., smaller than 0.1 µm, and the narrower the grain size distribution, the more effective is a polishing agent for the given region of rubbing resistance, because most of the grains in the size fraction actually do polishing. On the other hand, a broad grain size distribution which includes large grains is much less effective as a polishing agent, since only the larger grains actually contribute to the polishing.

The procedures described above can be used to produce CeO_2 polishing agents with defined characteristics with respect to the composition of individual grain fractions in narrow regions of just a few tenths of a micrometer on average and also with respect to rubbing resistance. Thus, there are cerium oxides that are appropriate for polishing of high-precision optics using low rubbing stresses as well as those that are appropriate for rapid polishing of optics of average quality using high rubbing stresses.

An example illustrating CeO_2 polishing agents of differing quality is shown in figure 3, which is a schematic diagram of the polishing efficiency (expressed as material removal) of two polishing agents, designated I and II. Polishing agent I is very effective at low shear (rubbing) stress, but shows no increase in efficiency at high shear stresses. Polishing agent II is very effective at high shear stresses, but is unusable at low stresses because of its extremely low efficiency at low stresses.

2.6 Determination of the amount of removal (polishing efficiency) of a polishing agent according to German standardization

A single number for the characteristic removal value of a glass by a polishing agent according to the German standard DIN 58 750 [40, pt. 3] is not sufficient for providing exact statements about the range of appropriate polishing conditions. Tests must be carried out under at least three very different sets of rubbing stresses in order to obtain curves such as those shown for polishing agents I and II in figure 3.

2.7 Determination of grain sizes, specifically for CeO_2 polishing agents

The grain size is a very important characteristic of a polishing agent. All companies which manufacture CeO_2 polishing agents determine grain sizes using sedimentation methods. However, as was discussed in detail in [15], no sedimentation method is appropriate for grain size analysis of grains smaller than about 0.05 to 0.5 µm, owing to the colloidal behavior of the very small particles. The sedimentation methods mentioned in DIN 58750 [40, pt. 1] can also not be used. The most certain way to determine grain sizes of the fine size fractions has proven to be a diameter calculation from a surface area measurement using the BET method, with a comparison of the average grain size using electron microscope photomicrographs.

3. Summary and conclusion

Using experimental results on the polishing efficiencies of model iron oxide polishing agents, it could be proven that the still-current hypothesis of the high hardness of polishing grains is not correct. Further, it could be shown that a gripping polishing agent must be softer than the material it is supposed to polish.

It was demonstrated that important characteristics of gripping polishing agents are the extra lattice defects that are built into the precursor materials in various ways, depending on the manufacturing path, as well as the high uniformity of the individual grains (narrow grain size distribution). Further, an oxide polishing agent must have an optimal shear strength or rubbing resistance or, as an equivalent, an optimal rubbing hardness for a particular range of polishing conditions. The optimal abrasion hardness values depend on the firing temperatures of the final products. It was reported how these temperatures are determined very exactly from the increase of the primary crystallite sizes and the decrease of the lattice defects with increasing calcining temperature. In addition, depending on the manufacturing path of a particular CeO_2 polishing agent, the calcining temperatures for the finer division of the shear strengths or rubbing resistances of the polishing agents can also be determined. An example was shown, i.e., the polishing efficiencies of polishing agents I and II in figure 3. It is suggested that the findings of this work be used in standards of properties of polishing agents.

The following conclusion can be drawn from the experiments presented above: The lattice defect theory of polishing agents leads to quantifiable values for the desired characteristics of the polishing agents as well as to methods by which these characteristics can be realized through knowledge and control of the manufacturing path for the most widely differing conditions of shear or rubbing conditions, i.e., for the most widely differing application ranges.

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