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(54) A process for obtaining a protective coating for surfaces subjected to mechanical and thermal wear, and coating obtained by such process.

(57) The process provides for coating surfaces (2) of elements (1) of heat engines subjected to wear by sliding and oxidation with a wear layer (3), and consists of a first electro-deposition phase performed in an aqueous electrolyte with a low hydrogen discharge, of a first layer (4) of hard chrome having a thickness lying between 20 and 40 μm and a hardness lying between 400 and 600 HV; and a second electro-deposition phase in an aqueous electrolyte based on a mixture of acids, of a second layer (5) of hard chrome over the first layer (4), having a hardness of at least 1000 HV and a maximum thickness of about 1.2 mm.

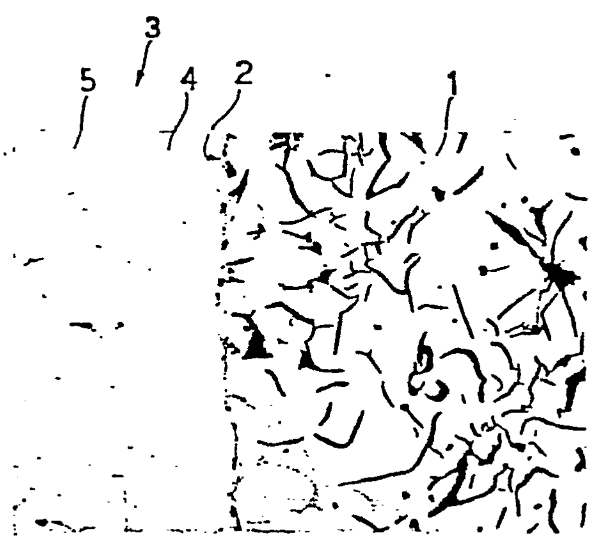

Fig.2

EP 0 147 484 A1

"A PROCESS FOR OBTAINING A PROTECTIVE COATING FOR SURFACES SUBJECTED TO MECHANICAL AND THERMAL WEAR, AND COATING OBTAINED BY SUCH PROCESS"

The present invention relates to a process for obtaining a protective coating for mechanical elements subjected to both thermal and mechanical wear, for example, subjected simultaneously to wear by sliding and friction and to oxidation, such as the surfaces of elements comprising the combustion chamber of a heat engine, for example, the cylinders, valve stems, piston crowns and, above all, piston rings. The invention further relates to a protective coating obtained by the process.

It is known that the components of modern heat engines, and in particular the elements of the combustion chamber of a diesel engine, are subjected to high thermal and mechanical stresses. In particular the sliding surfaces of the cylinders, pistons, valve stems and, above all, the piston rings, must have extremely high properties of resistance and thermal stability at high temperature, resistance to adhesive and abrasive wear and to seizure, to fatigue, to oxidation and to both chemical and electro-chemical corrosion, as well as to fretting. Such requirements have until now been at least partly satisfied by using for the said elements heavily alloyed cast iron covered with coatings of various types, both of the electro-plated type and the type obtained by flame or a coating obtained by plasma spray. Known electro-deposited coatings are principally obtained by means of coating a layer of chrome onto a base layer of nickel deposited on the surface to be protected. The thickness of the coating thus obtained does not exceed about 0.45 mm because layers of greater thickness would not be economic given the long deposition times required and, above all, because they would be incoherent, therefore causing a rapid flaking of the protective layer. The deposition processes are largely known, as are their operating parameters. They are usually performed in electrolytic baths of sulphate in aqueous solution, in the presence of chromium dioxide, with lead anodes and cathodes constituted by the work pieces to be covered, with a current density lying between 10 and 30 Ampere/dm^2 and a speed of deposition of about 20-25 micron/h.

Known electro-deposition processes are not entirely free from disadvantages. In particular they permit coating layers of only a small thickness which are not suitable to ensure a long life of the elements treated, which is necessary, on the other hand to be able to extend the maintenance intervals of the engines fitted with such elements. Further, there is a tendency these days, for reasons of economy, to use inferior fuels, rich in sulphur and other corrosive elements and which therefore cause a rapid corrosive wear of the protective layers,whether obtained by electro-deposition methods or with other methods,and of the elements protected thereby.

An object of the present invention is that of providing a process for obtaining a protective coating for surfaces subjected to wear, which will be free from the described disadvantages and in particular of greater thickness and resistance to chemical corrosion so as to be able effectively to protect the surfaces to which they are applied.

Another object of the present invention is that of providing such a protective coating by utilising electro-deposited coating layers.

The said objects are achieved by the present invention in that it relates to a process for obtaining a protective coating for surfaces subjected to wear by sliding and oxidation, in particular for surfaces of heat engines, characterised by the fact that it comprises:

- a first phase of electro-deposition onto the said surfaces of a first layer of hard chrome having a Vickers hardness lying between 400 and 600 Kg/mm^2 and a maximum thickness lying between 20 and 40 micron, the said first phase being performed in an electrolytic bath of aqueous electrolyte; and

- a second phase of electro-deposition onto the said first layer of hard chrome of a second layer of hard chrome having a Vickers hardness of at least about 1000 Kg/mm^2 and having a maximum thickness of about 1.2 mm the said second phase being performed in an aqueous electrolytic bath containing a mixture of acids and with a speed of deposition of the chrome from four to ten times greater than the speed of deposition of the chrome in the said first phase.

The present invention further relates to a protective coating for covering the surfaces of heat engines subjected to thermal and mechanical wear, in particular for elements constituting a combustion chamber of a diesel engine and particularly for piston rings and sealing rings of the pistons of reciprocating engines, characterised by the fact that it comprises at least:

- a first electro-deposited layer of hard chrome having a hardness lying between 400 and 600 HV and a maximum thickness lying between 20 and 40 micron, the said first layer being compacted and substantially free from cracks, micro-cracks and porosity; and
- a second electro-deposited layer of hard chrome overlying the said first layer and having a hardness of at least about 1000 HV and a maximum thickness of about 1.2 mm, the said second layer having a plurality of micro-cracks dispersed uniformly throughout and having dimensions lying between 5 and 30 micron and a distribution frequency in the said second layer of at least about 200 micro-cracks per linear cm.

For a better understanding of the present invention a non-limitative embodiment thereof will be described with reference to the attached drawings, in which:

Figure 1 illustrates a photograph on an enlarged scale of a section of a sealing ring for heat engine pistons, provided with a protective coating formed according to the invention;

Figure 2 illustrates a micro-photograph enlarged 500 times, of a base zone of the coating of Figure 1;

Figure 3 illustrates a micro-photograph enlarged 500 times, of an intermediate zone of the coating of Figure 1; and

Figure 4 illustrates a photograph on an enlarged scale of a section of a sealing ring such as in Figure 1, but provided with a protective coating formed with a known process.

With reference to Figure 1, an element of a combustion chamber for a heat engine is generally indicated 1, this being constituted, in the illustrated example, by a sealing ring for a diesel engine piston. The element 1, of which, for simplicity, only an outer portion of the radial section is illustrated, has a surface 2, in the illustrated example the outer side surface, subjected to wear both by sliding and oxidation, being intended to form a sliding seal between piston and the side wall of the cylinder of an engine in operating conditions. The surface 2 is provided with a protective coating 3 which acts to protect it both from mechanical wear and from thermal wear due to chemical and electro-chemical attack at high temperature by the combustion products.

The protective coating 3, in the illustrated example, comprises two superimposed layers, electro-deposited onto the surface 2; a first layer 4 of hard chrome, having a Vickers hardness of 536 Kg/mm^2 and a thickness of 35 micron (0.035 mm) deposited immediately in contact with the surface 2 of the element 1, which is made of cast iron; and a second layer 5 of hard chrome, having a Vickers hardness of 1073 Kg/mm^2 (1073 HV) and of thickness equal to 1.05 mm, deposited over the layer 4. As can be seen in Figures 2 and 3, the layer 4 is compacted, substantially free from cracks, micro-cracks and porosity, and adheres perfectly to the cast iron of the element 1. The layer 5 is perfectly adherent to the layer 4, free from blow holes and cracks, well formed and having instead a plurality of micro-cracks 6 of very small dimensions (Figure 3) lying between about 5 and 30 micron, uniformly distributed in the layer 5 itself.

More generally, the protective coating 3 formed according to the invention can be applied to any surface subject to thermal and mechanical wear; and in the field of engines not only the piston rings, but also the valve stems and the cylinder sleeves, and the piston crowns or cavities can be covered with this coating. The coating 3 can be made with a number of different variants, depending on technical requirements of the various applications, and therefore the layer 4 can have a maximum thickness lying between 20 and 40 micron and a hardness lying between 400 and 600 HV, whilst the layer 5 can have a hardness equal to or greater than 1000 HV and a maximum thickness equal to about 1.2 mm. In a variant not illustrated the coating 3 further comprises a third electro-deposited layer for running-in made of hard chrome deposited over the layer 5, of a hardness lying between about 650 and 800 HV and having a thickness such as to be completely worn away, leaving the layer 5 exposed, during the running-in phase of the engine the elements of which have had the coating 3 applied thereto.

The coating 3 has the dual function of constituting a protective layer for the surface 2 with regard to oxidising and chemically aggressive agents in general, and constitutes a consumable anti-wear layer for the surface 2. According to the invention this dual function is performed separately by the two layers 4 and 5. The layer 4, thanks to its high compactedness and excellent adhesion to the base material, whether it be cast iron or steel, guarantees the anti-corrosive and anti-oxiditive protection even in the presence of high temperatures (such as, for example, those in the combustion chambers of super-charged engines) and aggressive fuels such as heavy diesel having a high sulphur content. Thanks to its high thermal stability and to its capacity for rapid passivation, in fact, the chrome layer 4 prevents the formation of local electro-chemical corrosion pairs and the penetration of corrosive agents towards the base material.

The layer 5, on the other hand, serves to be slowly consumed during the operating life of the element 1 in such a way as to prevent direct sliding of the surface 2 and consequent possible gripping or seizure. Thanks to the great thickness (more than three times the normal thickness of electro-deposited chrome protective layers) it allows about three times the operating life of the element 1 permitting the maintenance intervals of the engines on which the elements provided with protective coatings 3 are fitted to be extended. One characteristic of this layer 5, as well as its thickness, is represented by the presence of the micro-cracks 6. These have dimensions such as to be able to collect and retain lubricating oil in such a way as to allow the formation of an internal oil reserve in the layer 5, which can be used in the event of critical lubrication conditions preventing any risk of seizure or damage to the protective coating 3. Experimental tests have verified that improved results of durability and adequacy of lubrication are obtained when the distribution frequency of the micro-cracks in the layer 5 is equal to or greater than about 200 microcracks per linear cm, which represents a critical value.

The protective coating 3 previously described is obtained with the following process.

After having proceeded with an accurate cleaning of the element 1 to be coated, there is deposited on the surface 2, by means of electro-deposition treatment, the layer 4 by operating in an electrolytic vessel with lead anodes and cathodes constituted by the elements to be coated, in an electrolytic bath containing chrome in solution, preferably as CrO_3, and chromic acid and with a voltage between the electrodes of between 4 and 10 volts. To obtain a layer 4 having the characteristics described, and therefore high compactedness, free from cracks and porosity, with good adhesion to the base metal, it is necessary however to operate in conditions with particular operating parameters, selected following a long experimenting period which has permitted, surprisingly, layers of electro-deposited chrome having the said characteristics to be obtained and which can be deposited with excellent adhesion directly on the base metal (cast iron or steel), without the interposition of an anchoring layer of nickel. These operating parameters consist in a high cathode current density, which must be maintained near to or equal to about 30 Ampere/dm^2, associated with a very slow deposition speed lying between about 5 and 15 micron/hour. The combination of these values allows an electrocrystallisation process to be obtained for the deposition, characterised by the presence of a very large number of nucleii of crystallisation and by crystals of very small dimensions; this permits the best characteristics of compactedness and adhesion of the chromium deposits to be obtained, which results in total impermeability to corrosive agents.

The hardness and thickness of the layer 4 can instead be chosen in dependence on the single coating requirements, by varying in a known way the duration of the deposition operation and the percentage composition of chrome in the bath; these must however remain between the following values:

- thickness of the layer 4: 20-40 micron
- Vickers hardness of the layer 4: 400-600 Kg/mm^2

After having obtained the layer 4 a washing operation is performed and then a second electro-deposition operation, this time utilising an aqueous electrolytic bath containing CrO_3 and a mixture of acids based on sulphuric acid (H_2SO_4) preferably mixed with hydrofluoric acid (HF) and possibly with other mineral acids.

The chrome layer 5 is deposited after the layer 4, acting in vessels with lead anodes and cathodes constituted by the elements to be treated and a voltage between the electrodes of about 5-15 volts. To obtain a great thickness of the layer 5, equal to more than three times the normally obtainable thickness, and simultaneously obtain a regular and compacted deposit, provided with micro-cracks 6, it has, surprisingly, been found that it is necessary to operate with an unusually high cathode current density, lying between 40 and 70 Ampere/dm^2 in combination with a speed of deposition which is also high, between four and ten times greater than the speed used for depositing the layer 4 and lying between 40 and 80 microns per hour. In this case, too, by varying the composition of the bath in a known way the hardness of the deposit, which must be greater than or equal to about 1000 kg/mm^2 (Vickers) can be determined. The maximum economic thickness of the layer 5 is of the order of 1.2 mm.

Optionally, a further electro-deposition operation can subsequently be performed by depositing on the layer 5 a further hard chrome layer of Vickers hardness lying between 650 and 800 Kg/mm^2 by working with a cathode current density of about 30-40 Ampere and a speed of deposition equal to that used in the deposition phase of the layer 5. This produces a layer having characteristics similar to those of the layer 5 but somewhat softer, which can be used as a running-in layer. Micro-cracks 6 can also be obtained in this layer.

From what has been described the advantages of the process according to the invention will be apparent. It allows chrome protective coatings of a new concept and very high characteristics of strength and durability to be obtained. Above all, the process described allows a chrome protective coating layer of great thickness to be obtained (a thickness greater than three times the thickness of current layers) in times substantially equal to those necessary to obtain conventional layers (of smaller thickness) with known processes, thanks to the high speed of deposition which is about three times that normally used. From a comparison between the photographs of Figures 1 and 4, respectively illustrating two electro-deposited chrome layers 5 of equal thickness, the first (Figure 1) deposited on a base layer 4 of pure chrome and with the process of the invention, and the second (Figure 4) with a conventional process onto a base layer of nickel, one can see how the chrome layer of Figure 4, because of the great thickness, has numerous macroscopic cracks which would in use lead to a rapid flaking of the layer itself.

(Prof. Ing. BONGIOVANNI Guido)

CLAIMS

1. A process for obtaining a protective coating (3) for surfaces (2) subjected to wear by sliding and oxidation, in particular for surfaces (2) of elements (1) of heat engines, characterised by the fact that it comprises:

- a first electro-deposition phase depositing onto the said surfaces (2) a first layer (4) of hard chrome having a Vickers hardness lying between 400 and 600 Kg/mm^2 and a maximum thickness lying between 20 and 40 microns, the said first phase being performed in an electrolytic bath of aqueous electrolyte; and
- a second electro-deposition phase depositing onto the said first layer (4) of hard chrome a second layer (5) of hard chrome having a Vickers hardness of at least about 1000 Kg/mm^2 and having a maximum thickness of about 1.2 mm, the said second phase being performed in an aqueous electrolytic bath containing a mixture of acids, and with a chrome deposition speed of four to ten times greater than the speed of deposition of chrome in the said first phase.

2. A process according to Claim 1, characterised by the fact that it further includes a third phase, subsequent to the said second phase, comprising electro-deposition of a running-in layer of hard chrome of Vickers hardness lying between about 650 and 800 Kg/mm^2.

3. A process according to Claim 1 or Claim 2, characterised by the fact that the said mixture of acids comprises principally sulphuric acid mixed with hydrofluoric acid.

4. A process according to any proceeding Claim characterised by the fact that the speed of deposition of the said first layer (4) lies between about 5 and 15 micron/hour.

5. A protective coating (3) for covering the surfaces (2) subjected to thermal and mechanical wear of elements (1) of heat engines, in particular for elements (1) constituting the combustion chamber of a diesel engine and particularly for piston rings and piston sealing rings of reciprocating engines, characterised by the fact that it comprises at least:

- a first electro-deposited layer (4) of hard chrome having a hardness lying between 400 and 600 HV and a maximum thickness lying between 20 and 40 microns, the said first layer (4) being compacted and substantially free from cracks, microscopic cracks and porosity, and
- a second electro-deposited layer (5) of hard chrome overlying the said first layer (4) and having a hardness of at least about 1000 HV and a maximum thickness of about 1.2 mm, the said second layer (5) having a plurality of micro-cracks (6) dispersed uniformly within it and having dimensions lying between 5 and 30 microns and a distribution frequency in the said second layer of at least about 200 micro-cracks per linear cm.

6. A coating (3) according to Claim 5, characterised by the fact that lubricating oil is collected and retained in the said micro-cracks (6).

7. A coating (3) according to Claim 5 or Claim 6, characterised by the fact that it further includes a third layer of hard chrome overlying the said second layer (5) and having a hardness lying between about 650 and 800 HV, having a thickness such as to wear completely during the running-in phase of the said heat engines.

8. A coating (3) according to Claim 6 characterised by the fact that it has been obtained by the process according to any of Claims from 1 to 4.

(Prof. Ing. BONGIOVANNI Guido)

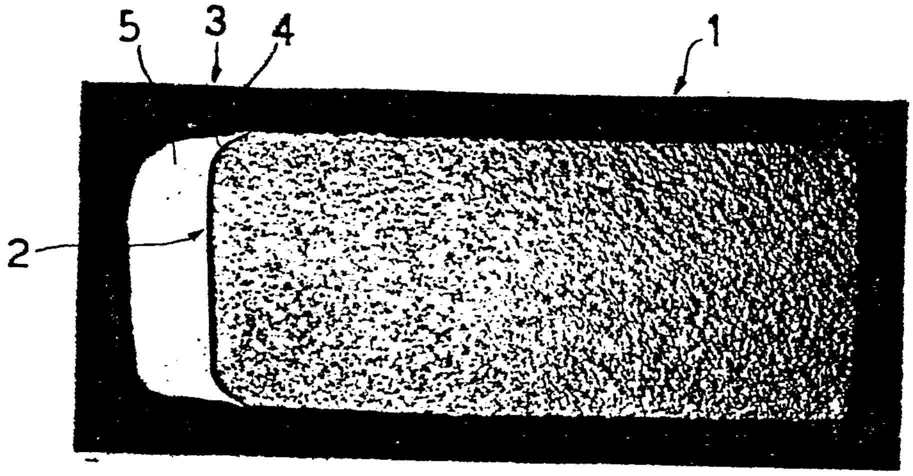

Fig. 1

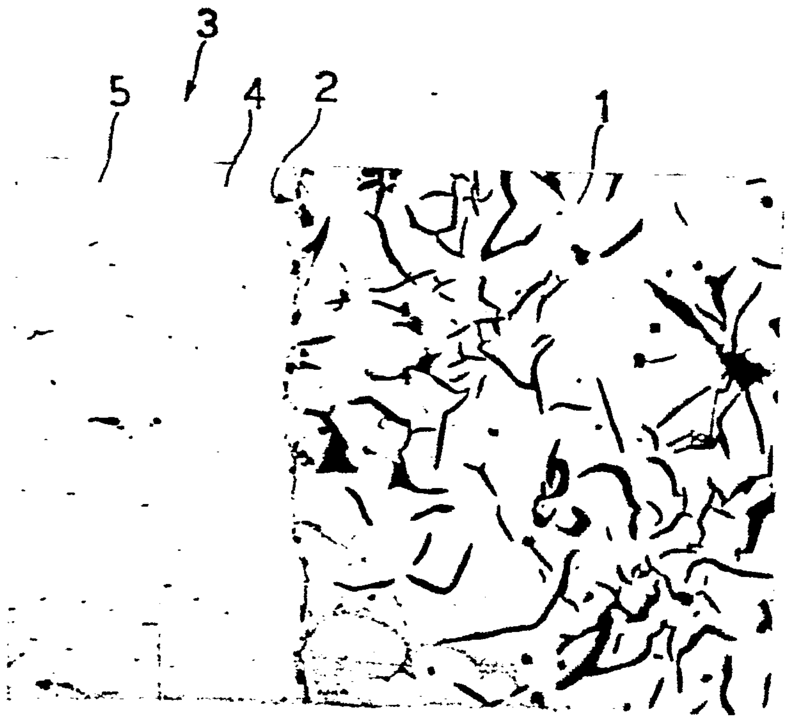

Fig. 2

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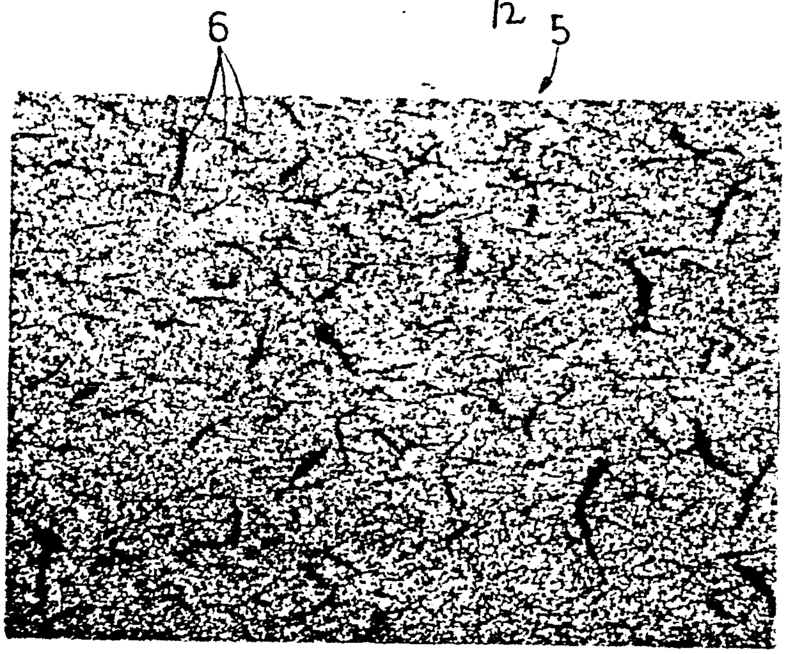

Fig. 3

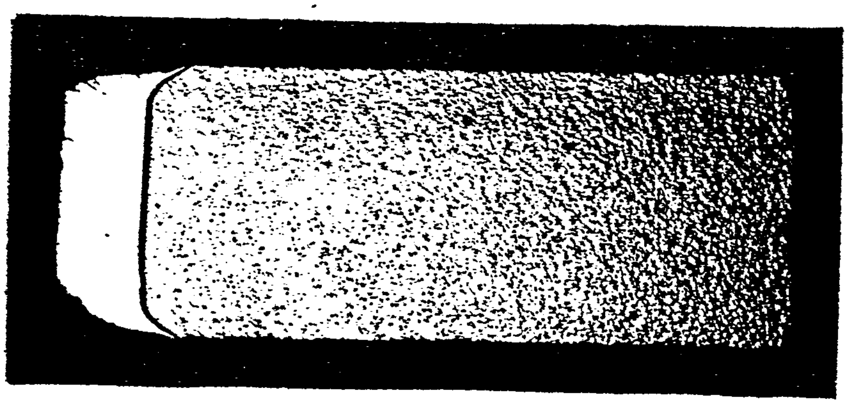

Fig. 4

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EUROPEAN SEARCH REPORT

0147484

Application number

EP 83 11 3249

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	DE-A-1 496 809 (GOETZEWERKE) ---		C 25 D 5/14
A	DE-A-1 521 079 (VOLKSWAGENWERK AG) ---		
A	CHEMICAL ABSTRACTS, vol. 92, 1980, page 504, no. 118542f, Columbus, Ohio, US; & JP - A - 79 117 335 (KOBE STEEL, LTD.) 12-09-1979 ---		
A	FR-A-1 301 720 (KATAYOSE) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 25 D 5/14 F 02 B 77/02 F 02 B 79/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28-09-1984	VAN LEEUWEN R.H.

CATEGORY OF CITED DOCUMENTS

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