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SINTERED ALLOY AND WEAR-RESISTING SLIDING PARTS MANUFACTURED THEREFROM

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ABSTRACT OF THE DISCLOSURE

A sintered alloy consisting of Fe, Cr, and Pb having a structure in which Pb is dispersed into a Fe-Cr-C matrix, and sliding parts or members manufactured from the sintered alloy.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to iron sintered alloys having excellent heat resisting and wear resisting properties employed for sliding parts or members, particularly for piston rings or valve seat rings of engines and particularly to sintered alloys having iron-chromium-carbon-lead components and sliding parts or members manufactured therefrom. Furthermore, a remarkable characteristic feature of the sintered alloy of the present invention resides in its self-lubricating property and accordingly, the sintered alloy of this invention has a favorable wear-resisting property against sliding motion even in lead-free gasoline.

Description of the prior art

Heretofore, for raw materials of sliding members, iron-carbon cast iron to which at least one alloying element such as boron, phosphorus, nickel, manganese, silicon, copper or chromium is added, or heat resisting steels have been employed.

Recently, for the purpose of improving the performance and durability of engines, a sliding member having excellent heat resisting and wear resisting properties has been requested and various improvements have been carried out in accordance with the requests. For example, a sliding member which is chromium-plated or molybdenum-coated with the above-mentioned alloy has been employed. Furthermore, a sliding member has also been fabricated by powder metallurgy processes, and the studies and developments of sintered alloy materials produced from iron-copper-carbon as the principal constituent and molybdenum, manganese, and silicon as the additional elements have also been carried out.

It became clear, however, that all of the above-mentioned sliding members were effective only in the case when they were used in conjunction wtih a conventional gasoline. That is, in conventional gasoline, a lead compound such as tetraethyl lead is added as an anti-knocking agent, but recently, pollution of the atmosphere due to lead in exhaust gases has become a problem and the development of lead-free gasolines and engines which can be used together with lead-free gasolines has continued.

Pb existing in gasolines presently employed serves also as a lubricant in the engine; particularly, Pb adheres to a contacting portion of the valve and the valve seat to thereby contribute to the prevention of seizure of these members and affords wear resisting properties thereto. Accordingly, when sliding members presently used are employed in conjunction with lead-free gasoline, the wear of the sliding members is accelerated which is undesirable. Therefore, in accordance with the development of gasolines in which the lead to be added is reduced or altogether removed, the development of sliding members having excellent heat resisting and wear resisting properties, and a high self-lubricating property has been eagerly sought.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a sintered alloy which can suitably be employed in sliding members having sufficient wear-resisting properties even when employed in conjunction with lead-free gasolines, excellent heat-resisting properties and favorable self-lubricating properties.

Another object of this invention is to provide sliding members such as piston ring members and valve seat ring members manufactured from the sintered alloy according to the present invention.

Still another object of this invention is to provide a process for producing the sintered alloy of the instant invention.

These objects can be attained by employing sintered Fe-Cr-C alloys which contain Pb in an amount of from about 0.2 to 20% by weight.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The nature, details, and utility of the invention will be more clearly apparent from the following detailed description beginning with general considerations and concluding with specific examples of practice constituting preferred embodiments of the invention and other examples for comparison and reference.

The sintered alloy of this invention is produced by blending C-powder, Fe-powders, and Pb-powder with an Fe-Cr alloy so as to obtain a predetermined compounding ratio of them, and then, the thus-blended mixture is sintered in an atmospheric gas. The amount of each component is 0.5–40% Cr, 0.1–3.0% C and 0.2–20% Pb, the remainder being Fe, each percent being by weight. Furthermore, when an alloy having a more remarkable heat resisting property is required, a small quantity of at least one element selected from the group consisting of Ni, Mo, Si, Mn, and Cu is added to the above described mixture and in this case, each element is added in an amount within the following ranges; that is, 0.5–20% Ni, 0.1–3.5% Mo, 0.05–3.0% Si, 0.05–5.0% Mn, and 1.0–30% Cu. Additionally, the mechanical and physical properties of the alloy may be adjusted or modified by adding a small quantity of Co, W, Ta, Ti, V, or Al to the above mixture.

The Cr component is added to and blended with the other components in the form of ferrochrome powder or other alloy powder and particularly, in the case when the Cr component is added in the form of Fe-Cr or Fe-Cr-Ni sigma-phase mother alloys, there is an advantage of easy manufacturing of a sintered body, that is, a sintered body having a high density can easily be obtained by only one compression molding and sintering process steps.

It is to be noted that Pb is not only contained in a mixture consisting of Fe-Cr alloy powders, Fe powder, and C powder prior to sintering, but also may be impregnated into a sintered body prepared by sintering the above described mixture. Ni and Mo are added to the mixture to be sintered in the form of sigma-phase mother alloy powder. Furthermore, additives or impurities other than those mentioned above may be included in the mixture insofar as the addition does not depart from the objects of the present invention.

In the following discussion, each component in the alloy will be more fully described. The carbon an essential element for imparting mechanical strength and wear resisting properties to the resulting product and in the case when the quantity of carbon added is less than 0.5%, remarkable improvements of mechanical strength and wear resisting properties cannot be observed. Further, in the case of adding less than 0.1% carbon, the improvement in the resulting product cannot be quite expected. On the other hand, in the case of adding more than 2.0% carbon, there is a slight tendency for the alloy to be brittle and in the case when the quantity of carbon is added in excess of 3.0%, the tendency becomes obvious. In the case when the sintered alloy of this invention is employed particularly for piston ring members in various sliding members, carbon within a range of 1.5–2.0% is added thereto and in the case when the alloy is used for valve seat ring members, the quantity of carbon added is suitably within a range of 0.1–3.0%.

The chromium combines with the carbon in the alloy to form carbide and a part of which solid solves with the iron thereby to elevate the heat resisting strength of the alloy, and furthermore, since a stable and thin oxidized film is formed on the surface of the alloy, it is effective for the prevention of oxidation and corrosion due to gas. In the case when the quantity of chromium added is less than 1%, the contribution thereof with respect to the improvement of the oxidation resisting properties and heat resisting strength becomes small, and in the case of less than 0.5% of chromium, the resulting sintered alloy is ineffective for piston ring members. Whereas, in the case when the quantity of chromium is more than 10%, there appears a tendency for the alloy to have a lower tenacity, and in the case of more than 40% chromium, a molded article having a sufficient strength can not be obtained because the compressibility of the powders are hindered. In the case when the sintered alloy of this invention is employed for piston ring members the quantity of chromium is within a range of 0.5–10.0%, and in the case of employing the alloy for valve seat ring members, a range of 1–40% is suitable.

The lead is effective for improving the mechanical workability of the alloy in the case when it is worked into each specific sliding member having a certain shape. Furthermore, when a sliding member is incorporated into an engine operating with lead-free gasoline, the lead dispersed in the matrix of an iron-chromium-carbon alloy exudes on the sliding surface to form a thin lubricating film, whereby the lead prevents seizure with the combined cylinder, smoothes the sliding of the ring, and effects the elevation of the wear resisting property of the sliding member. Additionally, in the case when minute dust is contained in a mixed gas consisting of gasoline and air and is held on a sliding surface, the dust is embedded into the soft lead existing on the sliding surface to thereby prevent the abrasion of the piston ring and cylinder liner due to grinding of the dust. In the case when the quantity of lead is less than 0.2%, the effects or advantages as mentioned above are poor, while when the quantity added is in excess of a value of 10.0%, there is a tendency that the mechanical strength of the alloy gradually decreases, and further, in the case when the quantity added is more than 20%, the alloy itself becomes brittle, and accordingly, it is not practical. In the case when the sintered alloy of this invention is employed for piston ring members, the quantity of lead is within a range of 0.5–10%, and in the case of valve seat ring members, a range of 0.2–20% is suitable.

The conditions for compression molding and sintering of the mixture will be generally described hereinbelow.

It is preferable that the mixture for sintering is subjected to compression molding under a molding pressure of 1.0–10 t./cm.^{2} and is sintered in a non-oxidizing gas atmosphere at a temperature of 1,150–1,350° C. In the case where the sintering temperature is lower than 1,150° C., diffusion of Cr is insufficient and an elevation of the wear resisting property can not be expected and on the other hand, when the temperature is higher than 1,350° C., scattering of Pb becomes remarkable and the lubricating effect becomes poor.

Furthermore, when the resulting sintered body is subjected to cold or hot forging, the following advantages are obtained.

(1) Pb or Pb compound contained in the sintered alloy exudes on the surface portion thereof, whereby the lubricating effect of the alloy becomes remarkable.

(2) A distribution of holes of the sintered body can be controlled and accordingly, the exudation degree of Pb can be also controlled.

(3) The exuded Pb is accumulated on the surface portion of the sintered body and as a result, the lubricating effect of the sintered alloy in lead-free gasolines becomes very remarkable.

For the above-mentioned forging conditions, a pressure range of 3.0–20 t./cm.^{2} is adopted and in this case, when the pressure is less than 3.0 t./cm.^{2}, the effect in elevation of density of the sintered alloy is poor and on the other hand, when the pressure is more than 20 t./cm.^{2}, the Pb in the alloy is pressed out therefrom and this attributes to a lowering of the lubricating property of the sintered alloy.

The sintered alloy of the present invention has a microscopic structure or texture such that lead of excellent self-lubricating property is caused to disperse into an iron-chromium-carbon alloy matrix having high heat resisting and wear resisting properties and mechanical strength. Therefore, when it is necessary to further elevate the heat resisting and wear resisting properties according to the conditions of use of the engine, the above-mentioned alloy elements of Ni, Mo, Si, Mn, Cu, etc. may be added thereto.

When the sintered alloy according to this invention has the ranges of components and constituents as mentioned above, the resulting alloy has a satisfactory mechanical strength, and sliding members having higher heat resisting and wear resisting properties and a more favorable self-lubricating property than those of conventional casting sliding members and sintered alloy sliding members can be economically manufactured. Furthermore, when the sliding members or parts manufactured from the alloy of the present invention are used in conjunction with gasolines to which no tetraethyl lead is added or other engine fuels, the sliding members of this invention have more favorable effects or advantages than conventional members as mentioned above.

As fully described above, when the sliding members according to this invention are compared with those made of a special cast iron and heat resisting steel presently used, the characteristic features of the former sliding members are remarkably elevated as piston rings and seat rings in lead-free gasoline. Furthermore, when the sliding members of the present invention are compared with those made of a simple sintered chromium steel, the wear resisting property is also elevated.

Moreover, it is, of course, to be noted that the sintering alloy according to the present invention is not only applicable for piston rings and seat rings, but also for other sliding members and wear resisting parts which are employed in an environment in which problems of corrosion and oxidation exist and at a high temperature, similar to which the above described piston rings and seat rings are employed in.

In order to indicate still more clearly the nature and utility of the present invention, the following specific examples of practice constituting preferred embodiments of the invention and results are set forth; it being understood that these examples are presented as illustrative only, and that they are not intended to limit the scope of the invention.

EXAMPLE 1

A mixture of a Fe 5%, Cr 1% and C composition, consisting of 40 wt. percent Cr-Fe sigma phase mother alloy powder (−325 mesh), Fe powder (−100 mesh), and carbon powder (−325 mesh) and another mixture having a composition of Fe 5%, Cr 1%, C 2% and Pb obtained by further adding lead powder (−100 mesh) to the former mixture were prepared, respectively. These mixtures were subjected to compression in metallic molds under a pressure of 6 t./cm.^{2} to obtain molded articles, respectively. When these molded articles were subjected to heating and sintering in a highly pure hydrogen atmosphere at a temperature of 1250° C. for 1 hour; tightening of the structures of the molded articles proceeded thereby to obtain sintered bodies of a high density, respectively.

Table 1 shows the characteristic features of values of the two molded articles as to their compositions, respectively.

TABLE 1

Composition	Specific gravity of— Molded article	Sintered body	HV hardness	Rockwell hardness
Fe 5%, Cr 1%, C	6.20	7.40	400	HRC 35
Fe 5%, Cr 1%, C 2%, Pb	6.30	7.50	380	HRC 30

EXAMPLE 2

A mixture of a Fe 5%, Cr 2.2%, Ni 0.43%, Mo 1%, and C composition, obtained by blending Fe 46 wt. percent, Cr 20 wt. percent, Ni 4 wt. percent, Mo sigma phase mother alloy powder (−325 mesh), Fe powder (−100 mesh), and carbon powder (−325 mesh) and another mixture having a composition of Fe 5%, Cr 2.2%, Ni 4.43%, Mo 1%, C–2%, and Pb obtained by further adding lead powder (−100 mesh) to the former mixture were prepared, respectively. These mixtures were compressed in metallic molds under a pressure of 6 t./cm.^{2} to obtain molded articles, respectively. The resulting molded articles were heated and sintered in a highly pure hydrogen atmosphere at a temperature of 1250° C. for 1 hour, respectively.

The following Table 2 shows the characteristic features or values of the two molded articles as to their compositions, respectively.

TABLE 2

Composition	Specific gravity of— Molded article	Sintered body	HV hardness	Rockwell hardness
Fe 5%, Cr 2.2%, Ni 0.43%, Mo 1%, C	6.25	7.45	450	HRC 40
Fe 5%, Cr 2.2%, Ni 0.43%, Mo 1%, C 2%, Pb	6.35	7.50	430	HRC 35

EXAMPLE 3

Seat rings manufactured from the sintered bodies produced in Examples 1 and 2, respectively, and other seat rings made of a Ni-Cr case iron or dies steel (SKD 1) and being commonly employed, respectively, were each incorporated into practical engines. Bench tests for 200 hours were carried out for the engines and the weights of the seat rings were measured before and after the tests, respectively. The heat resisting and wear resisting properties of these seat rings were estimated on the basis of each weight loss (percent) after test. The results of the tests will be shown in the following Table 3, respectively.

TABLE 3

Material	Weight loss (percent) Inlet side	Exhaust side
Fe 5%, Cr 1%, C	0.5	1.3
Fe 5%, Cr 1%, C plus 2%, Pb*	0.2	1.0
Fe 5%, Cr 2.2%, Ni 0.43%, Mo 1%, C	0.5	1.2
Fe 5%, Cr 2.2%, Ni 0.43%, Mo 1%, C plus 2%, Pb*	0.2	0.8
Ni-Cr case iron	1.0	4.0
Dies steel (first class)	1.0	2.5

*Sintered alloy of this invention.

EXAMPLE 4

A mixture having a composition of Fe 5%, Cr 1%, C 2%, and Pb was prepared by blending sigma phase mother alloy powder (Fe 40 wt. percent Cr) −325 mesh, iron powder −100 mesh, carbon powder −325 mesh, and lead powder −280 mesh. The resulting mixture was compressed in a metallic mold under a pressure of 6 t./cm.^{2} to obtain a molded article. The resulting molded article was heated and sintered in a highly pure hydrogen atmosphere at a temperature of 1250° C. for 1 hour.

EXAMPLE 5

A powdered mixture having a composition of Fe 2%, Cr 1.5%, C 4%, and Pb was prepared by mechanically mixing ferrochrome powder (Fe 63 wt. percent Cr) −325 mesh, iron powder −100 mesh, carbon powder −325 mesh, and lead powder −280 mesh, respectively. After the compression molding of the resulting powdered mixture under a pressure of 5 t./cm.^{2}, the thus-molded article was sintered in the same condition as in Example 4.

EXAMPLE 6

Sigma phase mother alloy powder (Fe 46 wt. percent, Cr 20 wt. percent, Ni 4 wt. percent Mo) −325 mesh, iron powder −100 mesh, carbon powder −325 mesh, and lead powder −280 mesh were blended in a compounding ratio of Fe 5%, Cr 2.2%, Ni 0.43%, Mo 6%, Pb 0.5%, C. The resulting mixture was subjected to compression molding under a pressure of 5 t./cm.^{2}, and then, the thus-molded article was sintered in an ammonium cracked gas at a temperature of 1200° C. for 1 hour.

For comparison with the sintered alloys of Examples 4–6, inclusive, conventional cast alloys and sintered alloys were tested as to the various characteristic features and wear resisting properties thereof. The condition of the test was such that each piston ring manufactured from each alloy was incorporated into a practical engine, and bench tests were carried out for the engine in a rotational frequency of 4,000 r.p.m. by the use of a regular gasoline (containing tetraethyl lead) at full throttle for 200 hours. After the test, the wear of each piston ring material was measured, the wear loss thereof being expressed by its worn dimension of the outer diameter of the ring and in this case, the cylinder to be combined with the above piston ring was made of a cast iron.

Furthermore, similar tests as mentioned above were carried out by replacing the regular gasoline with a lead-free gasoline and the wear of each piston ring was again measured. The results obtained will be shown in the following Table 4.

TABLE 4

Alloy	Tensile strength (kg./mm.^{2})	Hardness (HV)	Tested gasoline	Wear-loss (μ)
Example 4, Cr 5%, C 1.0%, Pb 2%, Fe remainder.	80	350	Lead-free	13
Example 5, Cr 2%, C 1.5%, Pb 4%, Fe remainder.	60	250	Regular	10
Example 6, Cr 5%, Ni 2.2%, Mo 0.43%, Pb 6%, C 0.5%.	100	400	Lead-free	8
Chrome plated cast iron, Si 2.5%, C 3.2%, Pb 0.3%, Fe remainder.	35	280	Regular	18
Do	35	280	Lead-free	50
Sintered material, Cu 3.0%, C 1.5%, Fe remainder.	37	200	do	55

NOTE.—A=Alloy of the present invention; B=Conventional alloy.

As is apparent from the results given in the Table 4, the sintered alloys according to the present invention have higher mechanical strength and hardness than those conventional ones and further, the wear resisting property of the alloy of this invention in either regular or lead-free gasolines is better than that of a conventional alloy.

EXAMPLE 7

A mixture having a composition of Fe 5%, Cr 1%, and C obtained by blending 40 wt. percent Cr-Fe of sigma phase mother alloy powder (−325 mesh), Fe powder, and carbon powder and another mixture having a composition of Fe 5%, Cr 1%, and Pb obtained by further blending lead powder (−280 mesh) with the former mixture were prepared, respectively. These mixtures were subjected to compression molding under a pressure of 6 t./cm.^{2} to obtain molded articles, respectively. These molded articles were heated and sintered in a highly pure hydrogen atmosphere at a temperature of 1250° C. for 1 hour to obtain sintered bodies having apparent specific gravities of 6.5 g./cc. and 6.55 g./cc., respectively. Both of these sintered chrome steels were heated in a nitrogen atmosphere at a temperature of 900° C. and pressed in metallic molds under a pressure of 12 t./cm.^{2}, respectively.

The characteristic properties of these two sintered bodies are shown in the following table.

TABLE 5

Composition	Specific gravity (g./cc.) of— Sintered body	Specific gravity (g./cc.) of— Hot compressed body	Seizure with metallic mold
(I) Fe 5%, Cr 1%, C	6.50	7.20	Seized after forging 2–3 bodies.
(II) Fe 5%, Cr 1%, C 2%, Pb.	6.55	7.40	Capable of continuous forging treatment.

NOTE.—(I)=Reference; (II)=This invention. Seizure with Metallic Mold indicates that in the case when a die forging is carried out by employing one forged metallic mold, how many forged bodies can be obtained without any seizure on the surface of the metallic mold.

As is apparent from the results shown in the above Table 5, in the sintered body of the Composition II containing Pb, the Pb or Pb compound exuded on the surface thereof at the time of its hot pressing and a lubricating film was formed on the surface of the sintered body. Accordingly, the antifriction effect of the sintered body having Composition II with respect to a metallic mold was remarkable and further, the increase of specific gravity of the compressed body having Composition II due to the pressure at the time of the hot pressing thereof was more remarkable than that of the sintered body having Composition I. Moreover, in the compressed body of Composition II, there was no seizure with respect to a metallic mold and accordingly, its continuous pressing was possible.

Abrasion tests were carried out in lead-free gasoline with regard to the sintered body having the above described Composition II and the results were as follows.

Conditions for test: Used internal combustion engine, 2 cylinder, 360 cc.: 7500 r.p.m. 4/4; gasoline used: lead-free gasoline (lead content of 0.002 g./gallon) having an octane No. of 90.

Result: The abrasion loss was 0.15 mm. for an endurance time of 70 hours.

What is claimed is:

1. A sintered alloy composition having good wear-resisting, heat-resisting and self-lubricating properties consisting essentially of a sintered powder mixture of carbon powder, iron powder, lead powder and an alloy powder selected from the group consisting of an iron-chromium alloy powder and an iron-chromium-nickel alloy powder, said alloy powder being in the sigma phase prior to sintering, wherein the lead is dispersed in an iron-chromium-carbon alloy matrix.

2. The sintered alloy of claim **1** consisting essentially of 0.5–40% by weight chromium, 0.1–3.0% by weight carbon and 0.2–20% by weight lead, the remainder being iron with the total being 100% by weight.

3. The sintered alloy of claim **2** consisting essentially of 0.5–40% by weight chromium, 0.1–3.0% by weight carbon, 0.2–20% by weight lead and 0.5–20% by weight nickel, the balance being iron with the total being 100% by weight.

4. The sintered alloy of claim **2**, consisting essentially of 0.5–40% by weight chromium, 0.1–3.0% by weight carbon, 0.2–20% by weight lead and 0.1–3.5% by weight molybdenum, the balance being iron with the total being 100% by weight.

5. The sintered alloy of claim **2**, consisting essentially of 0.5–40% by weight chromium, 0.1–3.0% by weight carbon, 0.2–20% by weight lead and 0.05–3.0% silicon, the remainder being iron with the total being 100% by weight.

6. The sintered alloy of claim **2**, consisting essentially of 0.5–40% by weight chromium, 0.1–3.0% by weight carbon, 0.2–20% by weight lead and 0.05–5.0% by weight manganese, the remainder being iron with the total being 100% by weight.

7. The sintered alloy of claim **2**, further consisting essentially of a small amount of at least one member selected from the group consisting of cobalt, tungsten, tantalum, titanium, vanadium and aluminum.

8. A piston ring member having good wear-resisting, heat-resisting and self-lubricating properties manufactured from a sintered alloy consisting essentially of a sintered powder mixture of carbon powder, iron powder, lead powder and an alloy powder selected from the group consisting of an iron-chromium alloy powder and an iron-chromium-nickel alloy powder, said alloy powder being in the sigma phase prior to sintering, wherein the lead is dispersed in an iron-chromium-carbon alloy matrix, said alloy consisting essentially of 1.5–2.0% by weight carbon, 0.5–10% by weight chromium and 0.5–10% by weight lead, the balance being iron with the total being 100% by weight.

9. A valve seat ring member having good wear-resisting, heat-resisting and self-lubricating properties consisting essentially of a sintered powder mixture of carbon powder, iron powder, lead powder and an alloy powder selected from the group consisting of an iron-chromium alloy powder, and an iron-chromium-nickel alloy powder, said alloy powder being in the sigma phase prior to sintering, wherein the lead is dispersed in an iron-chromium-carbon alloy matrix, said sintered alloy consisting essentially of 0.1–3.0% by weight carbon, 1–40% by weight chromium and 0.2–20% by weight lead, the remainder being iron with the total being 100% by weight.

10. A sintered alloy composition having good wear-resisting, heat-resisting and self-lubricating properties consisting essentially of a sintered powder mixture of carbon powder, iron powder, lead powder and an alloy powder selected from the group consisting of an iron-chromium alloy powder and an iron-chromium-nickel alloy powder, said alloy powder being in the sigma phase prior to sintering, wherein the lead is dispersed in an iron-chromium-carbon alloy matrix, said sintered alloy consisting essentially of 1–10% by weight chromium, 0.5–2.0% by weight carbon and 0.2–10% by weight lead, the remainder being iron with the total being 100% by weight.

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CERTIFICATE OF CORRECTION

Patent No. 3,758,281 Dated April 30, 1971

Inventor(s) Kenya MOTOYOSHI et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE HEADING:

Priority Data omitted. Insert the following:

Japan	No. 36998/70, filed April 30, 1970,
Japan	58175/70, filed July 2, 1970,
Japan	65178/70, filed July 25, 1970. --

Signed and sealed this 9th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

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Commissioner of Patents

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