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J. F. PELTON

3,846,084

CHROMIUM-CHROMIUM CARBIDE POWDER AND ARTICLE MADE THEREFROM

Filed Aug. 15, 1973

3 Sheets-Sheet 1

FIG. 1

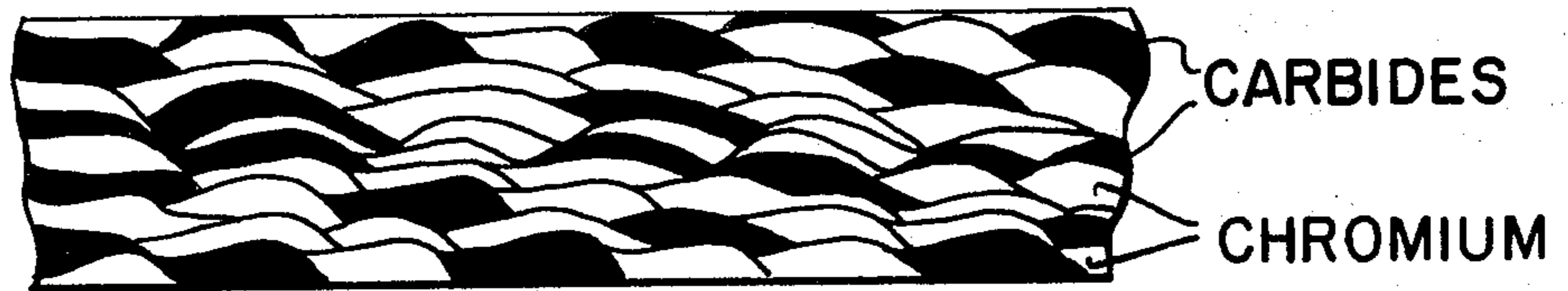


FIG. 2

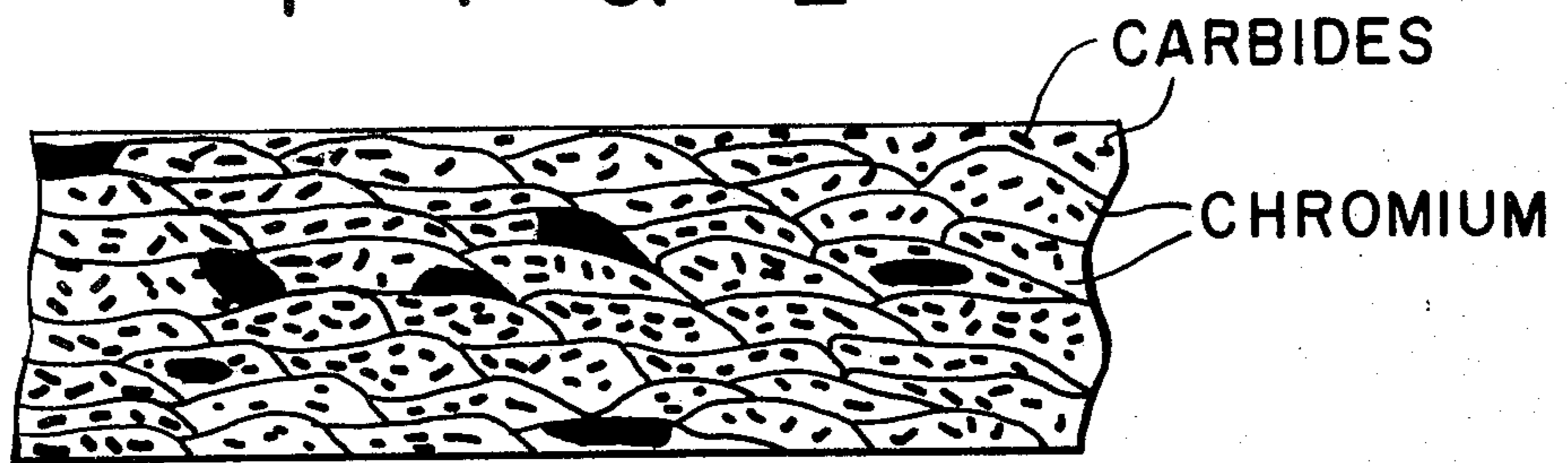


FIG. 3

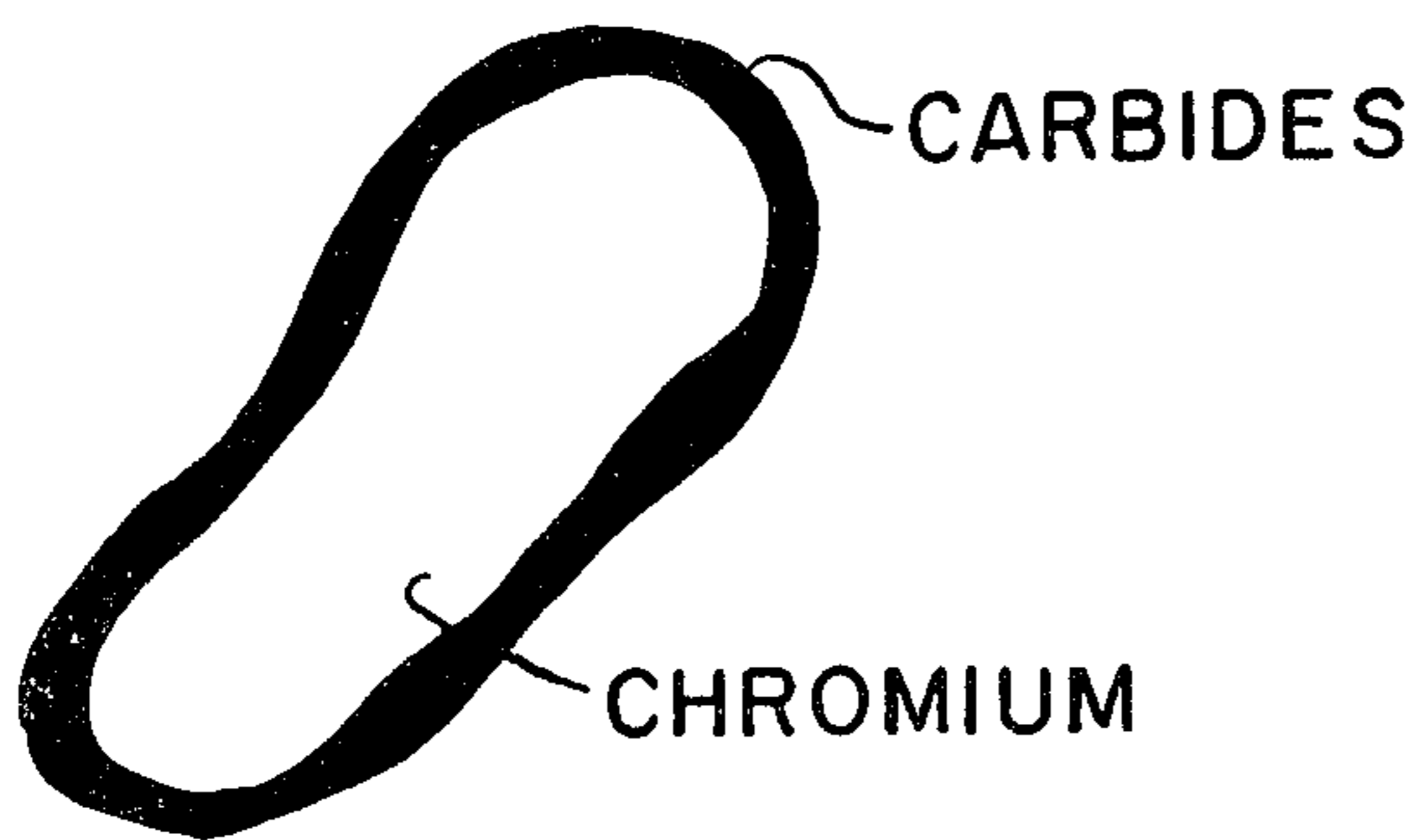


FIG. 4

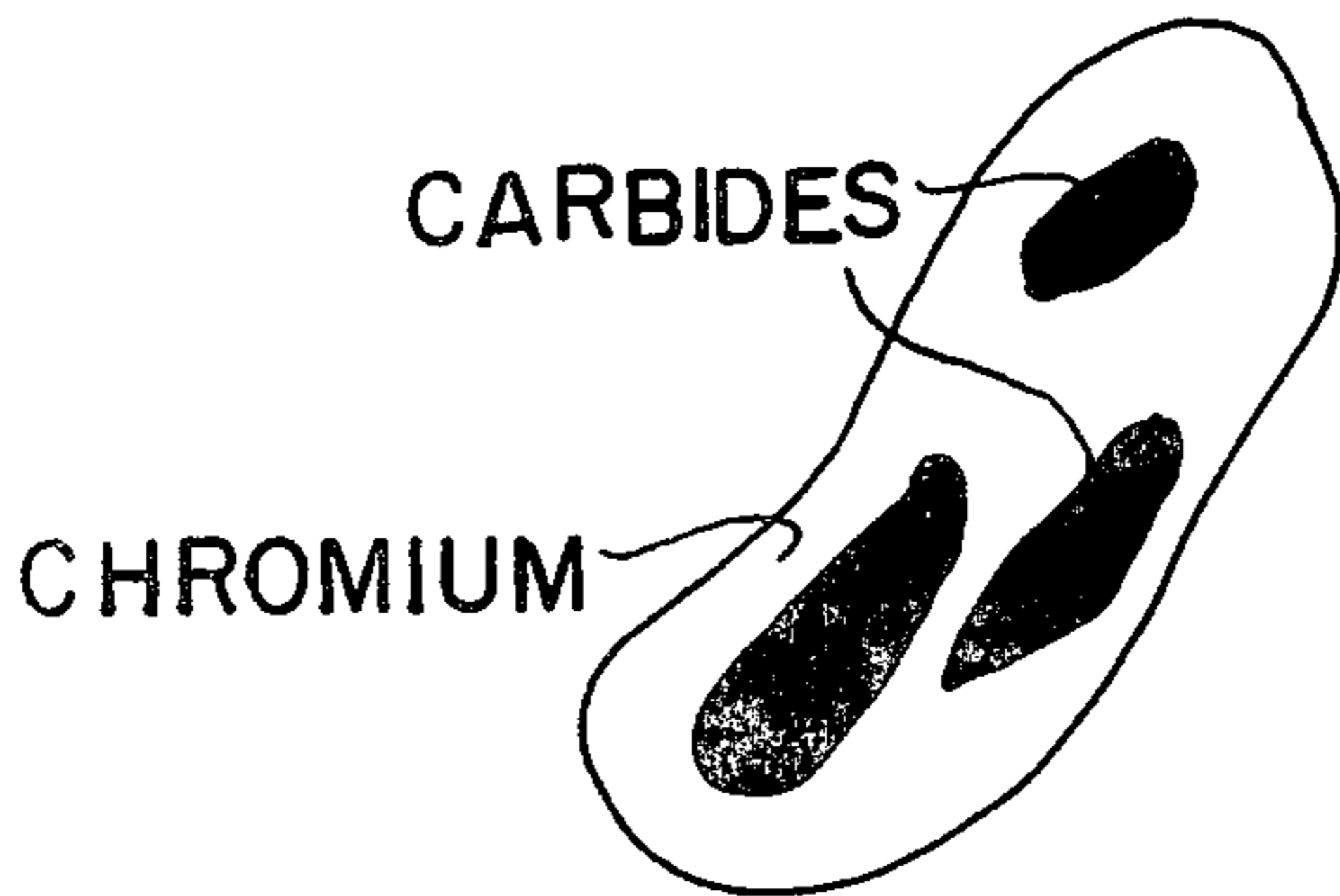
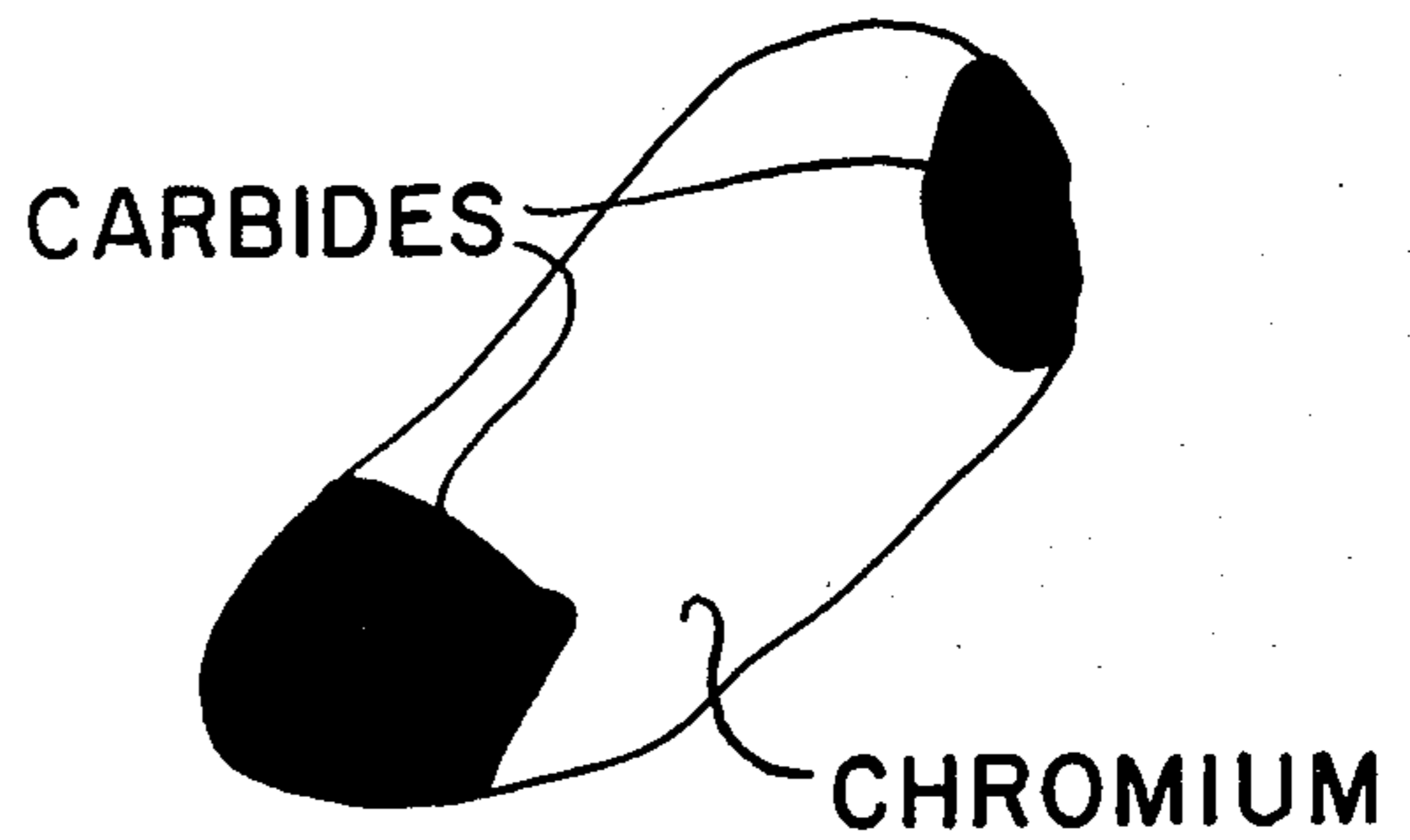


FIG. 5

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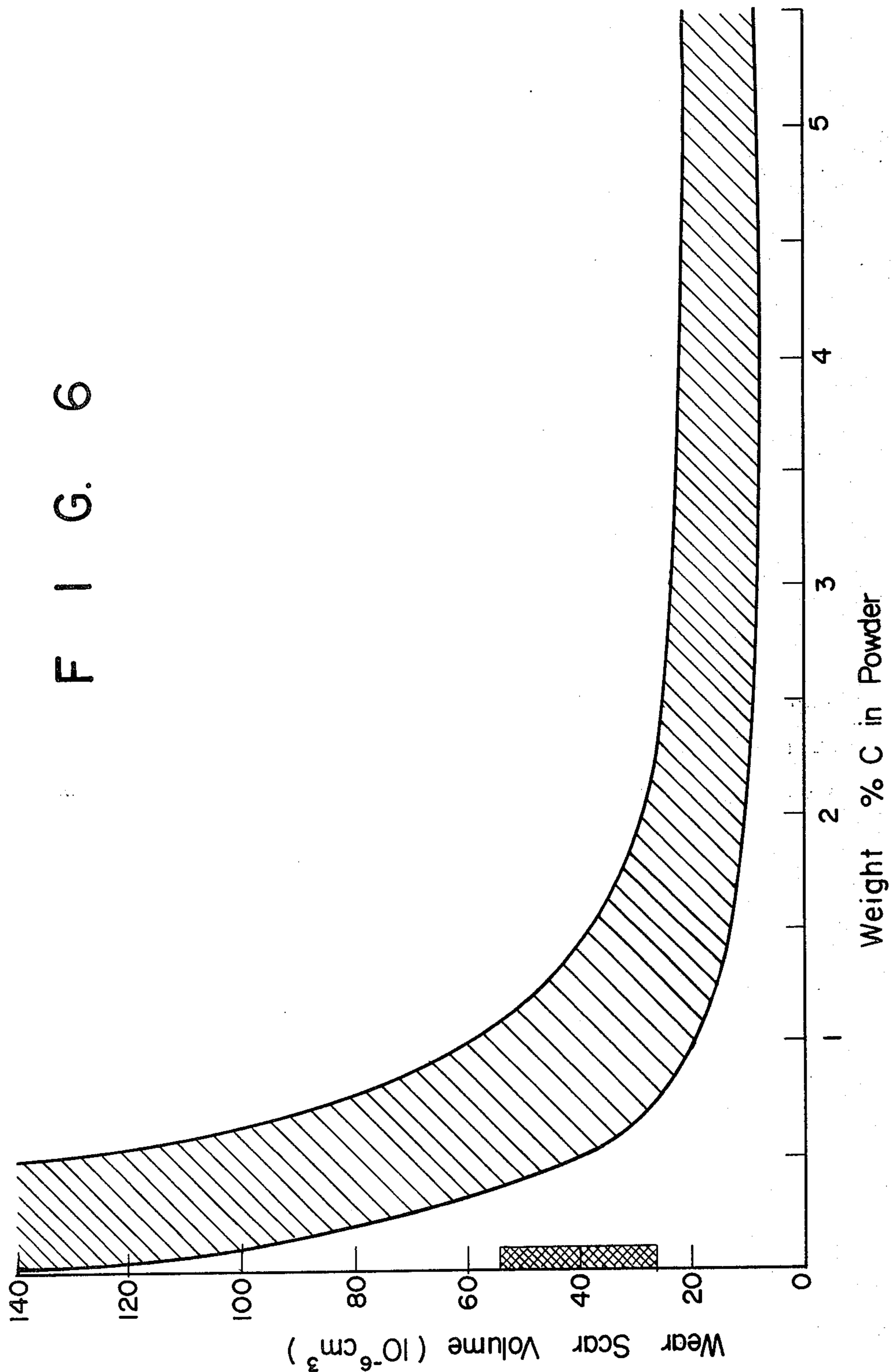
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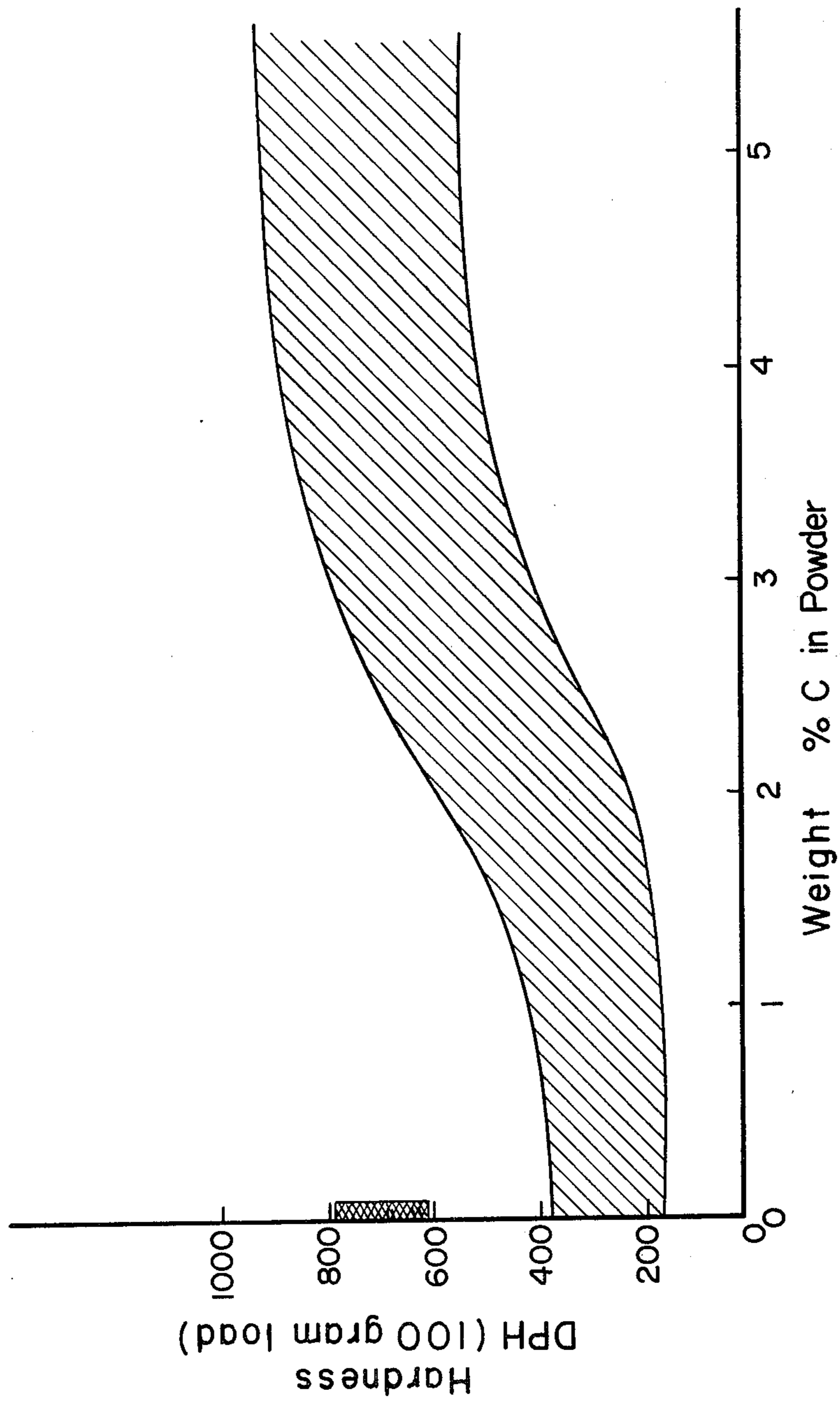
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## CHROMIUM-CHROMIUM CARBIDE POWDER AND ARTICLE MADE THEREFROM

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Int. Cl. B23p 3/00

U.S. Cl. 29—191.2

12 Claims

### ABSTRACT OF THE DISCLOSURE

A composite powder for use in producing articles or coatings having unique wear and frictional characteristics consisting essentially of a chromium matrix with at least one chromium carbide taken from the class of carbides consisting of  $\text{Cr}_{23}\text{C}_6$ ;  $\text{Cr}_7\text{C}_3$ ; and  $\text{Cr}_3\text{C}_2$  and each particle containing from about 0.2 wt. percent to about 5.4 wt. percent carbon.

Also described are processes for making the powder and an article coated by passing the powder through a plasma or detonation gun.

This invention relates to a novel powder for use in producing articles and coatings having unique wear and frictional characteristics. More particularly this invention relates to powders which are to be applied as a coating on a substrate using metal spraying techniques and to the articles and coatings made thereby.

Chromium metal has been used as an electroplated coating (i.e., "hard chromium plating") for many years to restore worn or damaged parts to their original dimensions, to increase wear resistance, reduce friction, and provide corrosion resistance. Chromium's excellent wear and frictional characteristics have been attributed to its low ratio of energy of adhesion to hardness when mated against a number of materials that are commonly used in engineering applications. Hard chromium electroplate, however, has a number of limitations. The electroplating of chromium is economically feasible when the configuration of the part is relatively simple and the number of the parts and/or their size is relatively small. When the configuration of the part becomes complex, obtaining a uniform coating thickness by electro-deposition is difficult and requires precise placement of electrodes and thieves. Without a uniform coating thickness, grinding to a finished surface configuration becomes necessary, and it is both difficult and expensive with electroplated chromium because of its inherent brittleness and hardness. The rate of deposition by electroplating is relatively low, and thus for a large number of parts and/or large areas and/or thick coatings a very substantial capital investment in plating tanks and power supplies is required. In chromium electroplating it is often necessary to use expensive surface cleaning and etching procedures to prepare substrates. Further, with many substrate materials it is not possible to directly apply chromium electroplating and one or more undercoats of other metals must be used. Spent plating baths present a disposal problem because they are a serious pollution source, and hence handling them adds significantly to the cost of the process.

An alternative method of depositing chromium metal is by metal spraying such as with a plasma or detonation gun. These methods offer a number of processing advantages. Surface preparation is relatively simple and inexpensive. The coatings can be applied to almost any metallic substrate without using undercoats. The rate of deposition is very high so that a large volume of parts can be coated with a minimal capital investment. The coating thickness can be controlled very closely so that any subsequent finishing can be kept to a minimum. The

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overspray can be easily contained and recovered making pollution control a simple matter.

Unfortunately, plasma-deposited chromium is not as wear-resistant at ambient temperature as hard electroplated chromium. This is because the wear-resistance of chromium plate is not an inherent property of elemental chromium but is believed to arise largely from impurities and stresses incorporated in the coating during plating. Plasma deposited chromium being a purer form of chromium thus lacks the wear resistances of hard chromium plate while retaining the corrosion-resistance characteristics of chromium.

It has now been discovered that coatings made by the plasma or detonation-gun process can be made that are remarkably superior to hard chromium electroplate in compatibility, frictional characteristics and wear resistance by incorporating a dispersion of chromium carbide particles in a chromium matrix.

Coatings of this type have been made from mechanical mixtures of powders as described in my co-pending application Ser. No. 388,434 filed Aug. 15, 1973. While such mechanical mixtures are advantageous, there are certain limitations to the quality of coatings made from them. Both plasma and detonation-gun deposition result in a coating with a multilayer structure of overlapping, thin, lenticular particles or "splats." Each coating particle or splat is derived from a single particle of the powder used to produce the coating. There is little, if any, combining or alloying of two or more powder particles during the coating deposition process. This results in some of the splats being completely chromium and some being completely chromium carbide, with the "finesness" or interparticle spacing being controlled by the sizes of the initial chromium and chromium carbide powder particles. Thus, the "finesness" of the chromium carbide dispersion in the coating is limited by the finesness of the powder that can be handled by the coating process. Since many desirable properties of the coating are improved by reducing the interparticle spacing or increasing the "finesness" of the dispersion and since it is desirable from a coating application standpoint to use powders with particles much larger than desired from the coating "finesness" standpoint, it would be advantageous to produce a coating in which each splat is a mixture of chromium and chromium carbide. This in turn requires that each powder particle contain a mixture of chromium metal and chromium carbide.

Accordingly, it is an object of this invention to provide a powder which, when sprayed by a plasma or detonation-gun, will produce an article or coating wherein each "splat" is a mixture of chromium metal and chromium carbides.

Another object is to provide such a powder which contains chromium and chromium carbide in each particle.

A further object is to provide a method for making such powder.

Yet another object is to provide a chromium/chromium carbide coating having superior property to hard chromium electroplate.

Still another object is to provide a coated trochoid surface for a rotary combustion engine.

These and other objects will either be pointed out or become apparent from the following description and drawings wherein:

FIG. 1 is a pictorial representation of the structure obtained by depositing mechanical mixture of chromium and chromium carbides;

FIG. 2 is a pictorial representation of the type structure obtained by depositing the powder of this invention;

FIGS. 3, 4 and 5 show possible distribution of the carbide phases in the powder particles;

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FIG. 6 shows the variation of wear scar volumes with carbon content of the powder used to produce the coating tested, compared to coatings of hard chrome plate; and,

FIG. 7 shows the hardness of coatings obtained with powders of various carbon content compared to hardness of hard chrome plate.

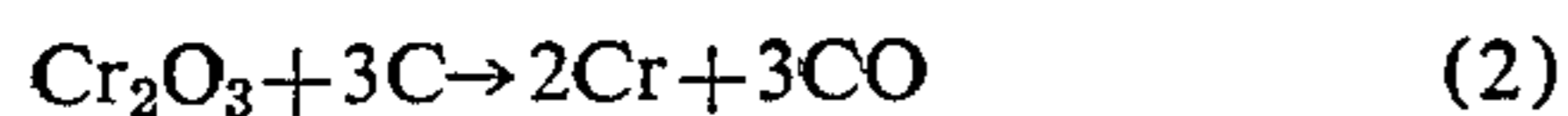
The methods of this invention, which will be described shortly, produce a composite powder containing the desired amount of chromium carbide and chromium in which substantially each particle contains at least some chromium and chromium carbide. Examples of the possible distributions of the carbide phases in the powder particles are shown in FIGS. 3, 4 and 5. For use in producing plasma or detonation-gun coatings, the exact composition of the carbide phases in the powder or the distribution of the carbide phases as shown in FIGS. 3, 4 and 5 are not important, only the total carbon content, since during deposition the particles become essentially completely molten. As the individual splats solidify during deposition, the carbides reprecipitate from the melt forming  $\text{Cr}_{23}\text{C}_6$ ,  $\text{Cr}_7\text{C}_3$ , or  $\text{Cr}_3\text{C}_2$ , or a combination of these, depending on the total amount of C present and the rate of solidification. The preferred composition results in a predominantly  $\text{Cr}_{23}\text{C}_6$  dispersion.

Basically, the material is prepared by chemical reaction of an intimate mixture of a source of Cr and a source of C; temperatures of 1000–1400° C. are suitable for solid state reactions. Times of from about 1–50 hours are suitable. Temperatures in excess of 1500° C. are required for production of the powder by melting referred to hereinafter. The principal reaction involved is



The principal product is  $\text{Cr}_{23}\text{C}_6$ , with minor amount of  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_3\text{C}_2$ .

When oxygen is present in the Cr (as  $\text{Cr}_2\text{O}_3$ ) or  $\text{Cr}_2\text{O}_3$  is used as the Cr source, reaction (1) is preceded or accompanied by



The Cr formed in reaction (2) may react with C present in excess of the amount required to bring reaction (2) to completion to form Cr carbide by reaction (1).

The source of Cr may be commercial Cr powder (e.g., Union Carbide Mining and Metals Division electrolytic chromium powder),  $\text{Cr}_2\text{O}_3$  as in reaction (2), or any compound that decomposes on heating or by reaction with C or  $\text{H}_2$  on heating to form essentially Cr and volatile products.

The source of carbon may be any commercial carbon consisting of essentially elemental C and volatile impurities. Decolorizing carbon, lampblack, and powdered graphite have been used with equal success. In addition, a higher carbide of Cr may be used as the C source, since it may react with Cr to form another carbide, the resulting product having the characteristic intimacy of the invention. As an example,

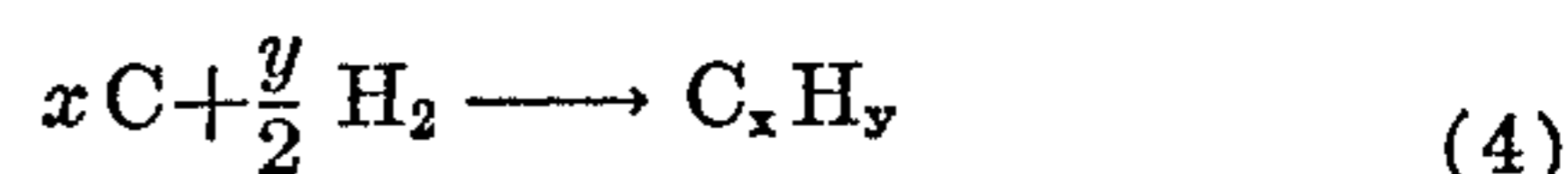


would produce a carbide on the surface of the Cr particles (present in excess of the amount consumed in reaction (3)).

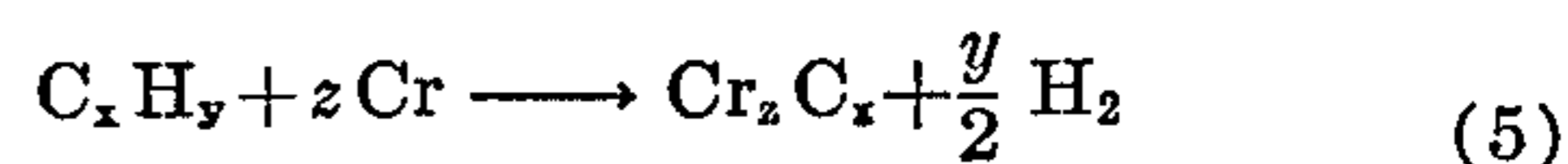
A gaseous hydrocarbon or hydrocarbon/hydrogen gas mixture is also a suitable carbon source, provided its composition is such that the carbon activity is high enough to permit carbide formation. This reaction has not been used directly, but powdered mixtures of Cr and C heated in a  $\text{H}_2$  atmosphere are found to consist, after reaction, of two-phase particles in which the carbide phase essentially encapsulates the original Cr particles as shown in FIG. 3. This structure differs from that found in similar mixtures heated in the absence of  $\text{H}_2$ , which show mainly isolated areas of carbide formation on the Cr particles, as shown in FIG. 4, corresponding to points of

## 4

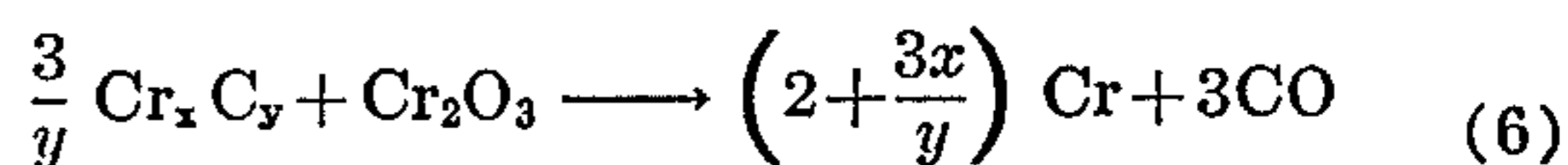
solid-solid contact of the original Cr and C particles. The difference in structure is clear evidence that carbon has been transported through the vapor phase in the  $\text{H}_2$  atmosphere, by the reaction



occurring at the carbon particles and the reaction



occurring at the Cr particles. This vapor transport reaction may be the principal source of Cr carbide formation or it may supplement reaction (1). Some oxygen removal reaction, either reaction (2) or reaction (6)



also occurs.

The intimately mixed Cr/Cr carbide structure may also be prepared by melting Cr and C (present either as the element or as a Cr carbide) mixtures of appropriate total analysis, allowing the homogeneous liquid to freeze and the Cr carbide to precipitate out, and then crushing the solidified melt to powder. Temperatures greater than 1500° C. are required for this method. Limitations of higher melting temperatures and difficulty in crushing the solidified melt practically limit this method of preparation to carbon content of 3% by weight or more.

The reaction of Cr and C is preferably carried out in vacuum because this promotes the removal of the gaseous CO formed in reaction (2) or (6). The vacuum does not have to be extraordinarily good, ultimate system pressures between 0.01 and 100 microns having been found to yield products of essentially the same oxygen content. The reaction can also be carried out in any atmosphere with oxygen potential sufficiently low to prevent oxidation of Cr. A hydrogen atmosphere is quite suitable and is particularly useful for the preparation of a composite of low C content with a uniform carbide distribution, since the  $\text{H}_2$  takes part in the reaction and promotes uniform distribution.

The product of the  $\text{Cr} + \text{C}$  or  $\text{Cr}_2\text{O}_3 + \text{C}$  reaction is a sintered cake, however the reaction is carried out. Sintering is least, and reduction to powder by ball-milling, hammer-milling, and other conventional techniques is easier, when the  $\text{Cr}_2\text{O}_3 + \text{C}$  reaction is used or when the  $\text{Cr} + \text{C}$  reaction is carried out in  $\text{H}_2$ . Lower reaction temperatures favor ease of reduction when the  $\text{Cr} + \text{C}$  reaction is carried out in vacuum.

The carbide distribution within the powder particle is a function of the method of production. When a mixture of solid carbon and chromium is heated in vacuum, the predominant form is that shown in FIG. 4 because the carbon tends to react with the chromium surface closest to it. The finer and more uniform the distribution of carbon in the starting mixture, the more uniform the distribution of carbides around the surface of the chromium will be. The ultimate extension of this trend is achieved when a gaseous source of carbon is used either by directly supplying a hydrocarbon gas or by heating the solid carbon plus chromium in a hydrogen atmosphere (which results in a hydrocarbon gas). The carbide distribution which results is like that in FIG. 3. A distribution of carbon particles throughout the powder particle, FIG. 5, may result when a solid ingot of the proper total composition is reduced to powder.

Oxygen content (in the range 0.03 to 1%) does not affect the wear properties of coatings made from powders of this invention. The carbon content of the powder of this invention may be between 0.2% and 5.4% by weight. At the lower limit, plasma deposits made from the powder are superior in tests to similar deposits made from commercial electrolytic chromium powder. The high end of the range is defined by the complete conversion to the

compound  $\text{Cr}_{23}\text{C}_6$ , which contains 5.6% by weight; at this point, the material no longer contains free Cr. The wear resistance of coatings made from the powder varies with carbon content as shown in the band curve on FIG. 6. The range of values observed for commercial hard chrome plate is also shown in the FIG. 6 by the cross-hatched area adjacent to the vertical axis.

The optimum composition is believed to lie in the range 0.8–1.7% C. by weight, and may vary somewhat with the method of preparation. Coatings, made from powders in this composition range, are equivalent to or superior to commercial electrolytic Cr plate in laboratory lubricated rubbing wear tests at high load (see FIG. 6). Furthermore, the hardness, see FIG. 7, is at a minimum, making it possible to readily finish the coating with conventional grinding or honing tools. Low-surface-speed, high-deposition-rate plasma plating produces well-bonded, uncracked coatings.

Specifically, it has been found that powders containing about 1 wt. percent carbon produce plasma deposited coatings on interior trochoid surfaces of rotary combustion engines which have remarkably and unexpectedly superior properties, as shown hereinafter in Example 9.

The coating of this invention is characterized by the presence in substantially every splat of both Cr and Cr carbide. As pictorially illustrated in FIG. 2, the relative amounts of Cr and Cr Carbides will vary between splats as a necessary result of the use of powder with a range of partial sizes and adventitious difference in the degree to which each Cr particle is carburized and in the conditions to which the various particles are subjected in passing through the coating device. Nevertheless, the coating of this invention is distinguished from that produced from a powder which is a simple mixture of Cr and Cr carbide, which is pictorially represented in FIG. 1, in that the splats in the latter type of coating are each individually either all Cr or all Cr carbide.

FIG. 2 is to be understood as being merely illustrative of one feature of the distribution of the carbides in the coating. Upon extraction by chemical methods of carbides from the invention and examination of these carbides by optical and electron microscopy, it has been found that at least some, and probably most, of the carbides are much finer than suggested by FIG. 2. The majority of the carbide particles were found to be of sub-micron size and most were predominantly in the shape of a lace-like network, suggesting that the coatings contained fine-grained interlocking, continuous networks of both carbide and Cr, the separation between the interstices of these networks being so small that they are not resolvable in optical microscopy.

The coatings produced with the powder of this invention have a number of advantages in addition to the general processing advantages previously described as being associated with metal spray deposition.

(1) Coatings are superior to those formed by the plasma deposition of commercial electrolytic chromium powder in that increased wear resistance and resistance to spalling are found, though there is minimal increase in hardness as measured by diamond pyramid indentations.

(2) Coatings are superior to coatings in which nitrogen rather than carbon is the strengthening additive, in that carbide-strengthened material is much less brittle and much less prone to spalling.

(3) In the laboratory lubricated rubbing wear test described in Example I, the coatings of this invention with a carbon content in the preferred range of 0.8–1.7 wt. percent C, performed as well as or better than commercial electrolytic chrome plate.

(4) Coatings of this invention performed far superior to electrolytic chrome plate coating on internal trochoid surfaces in rotary combustion engines as described in detail in Example 9.

The following examples illustrate the invention but are not intended to limit the variations in processing that

would be apparent to those skilled in the art. Moreover, the use of the powder of this invention is not intended to be limited to plasma or detonation-gun deposition.

#### EXAMPLE 1

8879 grams of Union Carbide Mining and Metals Division electrolytic chromium, screened through a 230-mesh sieve, was mixed with 200 grams of Fisher Scientific Company Norit A decolorizing carbon, similarly screened, and blended for two hours in a cone blender. A portion of this mixture was used to fill eight pans, each about 0.6 cm. deep, so that each pan contained between 210 and 230 grams of the mixture. The pans were vertically stacked in a vacuum furnace so that there was about 0.4 clearance between pans. The furnace was evacuated slowly to about 500-micron pressure and then more rapidly to about 0.5 micron, using an oil-diffusion pump. Power was then applied to tantalum strip heaters surrounding the stack of pans and the pans heated over a period of about 80 minutes to a temperature of  $1080^\circ\text{C}$ . as indicated by a thermocouple in contact with the powder in the uppermost pan; system pressure was maintained below 50 microns during this period by adjusting the rate of heating. The powder was maintained at  $1080^\circ\text{C}$ . for four hours, during which time the pressure gradually dropped to about 0.3 micron. The furnace was then allowed to cool to room temperature with pumping continued. When the pans were removed from the furnace, the material was in the form of sintered cakes of a significantly more metallic appearance than the original powder mix. These cakes were crushed in a mechanical pulverizer until about 95% of the material was reduced to powder that would pass a 325-mesh screen. The balance of the original mixture of chromium and carbon powders was processed identically in four additional furnacings.

The -325 mesh powders from the five furnace runs were individually analyzed for combined carbon, free carbon, and oxygen. All showed less than 0.1% free carbon, between 300 and 420 p.p.m. oxygen, and 1.05–1.08% combined carbon. The distribution of carbides on the chromium was similar to that in FIG. 4.

The products of the five runs were blended together and used to produce coatings by deposition through a plasma torch. Coatings so produced, when separated from the substrates on which they were plated, analyzed 1.03–1.06% C. The wear resistance of these plasma-deposited coatings were measured using a Dow-Corning LFW-1 Friction and Wear Test Machine according to ASTM Standard Method D2714-68. Coatings deposited 12 mils thick on the wear surface of mild steel wear blocks were ground to a final thickness of 5 mils and tested against carburized AISI 4620 steel rings (surface hardness 58–63 Rockwell "C") at 450 lb. specific load for 5400 ring revolutions at about 180 r.p.m.; MIL-5606A hydraulic fluid was used as lubricant. Wear scar volumes, calculated from the projected scar areas and the known ring diameter, ranged between  $24$  and  $49 \times 10^{-6}$  cm.<sup>3</sup>. These test results are included in FIG. 6.

#### EXAMPLE 2

Numerous mixtures differing only in the amounts of electrolytic chromium and decolorizing carbon used were processed as described in Example 1. The resulting powders, which ranged in carbon content from 0.6 to 5.4%, were used to form plasma-deposited coatings and tested for wear resistance using the techniques and procedures described in Example 1. Results of these tests are included in FIG. 6.

#### EXAMPLE 3

5400 grams of the same electrolytic chromium powder used in preceding examples was mixed with 87 grams of lampblack for one hour in a ceramic ball mill and then further mixed for 30 minutes in a cone blender. The mixed powders were loaded into pans and heated in the

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vacuum furnace exactly as described in Example 1. The product, after reduction to -325 mesh powder, analyzed 0.81% carbon and 335 p.p.m. oxygen. Plasma-deposited coatings were made and tested as described in Example 1. Scar volumes of 21 to  $34 \times 10^{-6}$  cm.<sup>3</sup> were observed; these results are included in FIG. 6.

## EXAMPLE 4

1476 grams of the same electrolytic chromium powder used in previous examples and 24 grams of the same screened decolorizing carbon used in previous examples were blended for two hours in a cone blender. Two boats, each 0.6 cm. deep and about 25 cm. long, were filled with this powder and placed in a 10 cm. diameter ceramic tube furnace which was then sealed and evacuated with a mechanical pump for several hours. The furnace was then filled with hydrogen, heated to 1150° C., and maintained at this temperature for 22 hours, a flow of 15 s.c.f.h. of hydrogen being maintained during the entire cycle. The product was a sintered cake much more readily reduced to -325 mesh powder than the products of the vacuum processing previously described. This powder analyzed 1.06% carbon, 630 p.p.m. oxygen. Plasma-deposited coatings made and tested as described earlier had scar volumes of 21 to  $42 \times 10^{-6}$  cm.<sup>3</sup>. A portion of the powder was mounted and polished to metallographic examination; at 500× magnification, it appeared that most, and possibly all, of the powder particles consisted of a shell of chromium carbide surrounding a core of chromium metal similar to that in FIG. 3. In this respect, the structure differed from that of powders prepared by vacuum processing; in the latter carbide and metal were observed in the same particles, but complete encapsulation was not observed.

## EXAMPLE 5

1773 grams of the same electrolytic chromium powder used in previous examples and 27 grams of the same screened decolorizing carbon used in earlier examples were blended by shaking and rolling in a 32-oz. glass jar. Using this powder, eight separate heats, each with between 80 and 105 grams of mix, were made in a 4 cm. diameter tube furnace. Each heat was for five hours at 1140° C. in a flow of about 110 s.c.f.h. hydrogen without preliminary evacuation. The eight cakes were easily powdered by light hammering and when blended together and screened yielded a -325 mesh powder containing 1.13% C. and 1730 p.p.m. oxygen. The microstructure of this powder was very similar to that of the powder described in Example 4, consisting of chromium carbide surrounding chromium; in addition, a small amount of very fine precipitates was noted decorating the carbide-chromium interface.

## EXAMPLE 6

A powder analyzing 1.13% C prepared by the method described in Example 1 was plated onto test blocks using a detonation gun. Microstructural differences between these coatings and those formed by plasma deposition were observed consistent with the difference in method of coating formation. For wear-test conditions identical with those employed for the plasma-deposited materials, scar volumes of  $15-19 \times 10^{-6}$  cm.<sup>3</sup> were measured on the detonation-gun coatings.

## EXAMPLE 7

Four hundred lb. of Cr<sub>2</sub>O<sub>3</sub> was blended with 94.8 lb. of lampblack in a twin-shell blender and then more thoroughly blended in a vibratory ball mill. This product was then mixed with 9.5 lb. cornstarch binder and enough water to make a mix suitable for forming briquettes in a standard briquetting press. It was then pressed into briquettes of about 2-inch maximum dimension and dried to remove excess water. The briquetted mix, charged to a large vacuum furnace in an 19-inch-deep bed covered with graphite plates, was heated to 1000° C. without let-

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ting the pressure exceed 5000 microns, held one hour at 1000° C. after the pressure had dropped below 2000 microns, then heated to 1400° C. and held at that temperature for 50 hours, at the end of which time the pressure had dropped to less than 150 microns. A portion of this product was pulverized to -325 mesh size and found to contain 1.14% C and 460 p.p.m. oxygen. The carbide dispersion in the powder was similar to FIG. 4. Wear samples formed from this material by plasma deposition and tested as described previously exhibited wear scars of  $21-24 \times 10^{-6}$  cm.<sup>3</sup> volume.

## EXAMPLE 8

A mixture of 9900 grams of commercial grade electrolytic chromium sized to pass through a 65-mesh screen and 100 grams of lampblack was blended dry, then mixed with water and cornstarch binder and formed into briquettes as described in Example 7. The briquetted mixture was then furnace in vacuum under graphite covers for one hour to 1000° C. and for eight hours at 1385° C. The pressure in the furnace was maintained below 500 microns and was 50 microns at the end of the heating period. This material was then crushed, yielding about 30% -325 mesh material that analyzed 1.3% C and 721 p.p.m. oxygen, with a carbide dispersion similar to FIG. 4. Wear samples made from this powder by plasma deposition and tested in the standard manner exhibited wear scars of  $18-23 \times 10^{-6}$  cm.<sup>3</sup>.

## EXAMPLE 9

Plasma deposited coatings produced in a manner similar to Example 1 were applied to the interior trochoid surfaces of rotary combustion engines fitted with graphite-aluminum composite rotor apex seals. The engines were run in laboratory test stands and in test vehicles. The trochoids were made of several different types of materials and of two different sizes, examples of which are shown in Table I. Over 3113 hr. of test stand operation have accumulated on the small engine size and 331 hr. of test stand and 7000 hr. of vehicle operation on the large engine size. In comparison with hard electroplated chromium the coatings of this invention showed the following advantages:

(a) Essentially no wear of the coated surface has been observed and no roughening or "wash boarding," as occurs with electroplated chromium, has developed.

(b) The wear of the mating seal surface is approximately one-half that caused by hard electroplated chromium, which is greater than .005" per 100 hr.

(c) Performance of the coating is less sensitive to surface finish than hard electroplated chromium. There was no appreciable difference in wear of either the coated surface or the seal surface between as-ground coating surfaces of 16 to 32 microinches rms and honed surfaces of approximately 6 rms. In comparison, a hard electroplated chromium surface must be finished to better than 6 microinches rms to perform satisfactorily.

(d) Finishing of the plasma-deposited coating is far simpler and may be cheaper since it can be used as-ground while a hard electroplated chromium coating must be ground, then etched to enhance the micro cracked texture of the surface, and then honed to improve the surface finish. Because thickness control is better with plasma deposition than with electroplating, the amount of material that must be removed in finishing is also less.

(e) The performance of engines with the coatings of this invention is far less sensitive to fluctuation in coolant temperatures than those coated with hard electroplated chromium.

(f) The performance of engines with the coatings of this invention is far less sensitive to fluctuation in oil lubrication than that of engines coated with hard electroplated chromium. The latter require continuous addition of oil to the combustion chamber, but an engine provided with the coating of this invention continued to perform satisfactorily when the oil addition was stopped.

(g) The cost of engines and the vehicles can be reduced using the coatings of this invention because they can be applied directly to aluminum trochoid housings while the use of hard electroplated chromium requires a steel liner. This reduces not only the cost of the housing, but also the weight of the engine and therefore the cost of vehicle frame, suspension, etc. In addition, engine cooling is more efficient. With lower total vehicle weight, fuel efficiency is increased.

TABLE I

Trochoid type	Trochoid size <sup>1</sup> (in.)	Coating thickness (in.)	Total time of test (hr.)	Average seal wear rate (in./100 hr.)
Aluminum with—				
Steel liner.....	9.5 x 7.1 x 2.75	.015-.017	800	.0026
No liner.....	9.5 x 7.1 x 2.75	.019-.020	444	.0026
Steel liner.....	11.5 x 8.6 x 2.75	.018-.015	220	.0026
No liner.....	11.5 x 8.6 x 2.75	.016-.018	76	.0026
Cast iron.....	9.5 x 7.1 x 2.75	.010-.0115	200	.006

<sup>1</sup> Major axis x minor axis x width.

Having described the invention with reference to certain preferred embodiments, it should be understood that minor modifications can be made thereto without departing from the spirit and scope thereof.

What is claimed is:

1. A powder containing from about 0.2 wt. percent to about 5.4 wt. percent carbon and wherein substantially every particle of said powder consists essentially of chromium and at least one chromium carbide taken from the class consisting of  $Cr_{23}C_6$ ;  $Cr_7C_3$  and  $Cr_3C_2$ .

2. A powder according to Claim 1 wherein said powder contains from about 0.8–1.7 wt. percent carbon.

3. A powder according to Claim 1 wherein said powder contains about 1 wt. percent carbon.

4. A powder according to Claim 1 wherein each particle has a core of chromium substantially completely surrounded by a shell of said chromium carbides.

5. A powder according to Claim 1 wherein each particle contains chromium and said chromium carbides on the surface of said chromium.

6. A powder according to Claim 1 wherein each particle contains chromium and said chromium carbides dispersed within said chromium.

7. An article consisting of a metal substrate having a coating thereon consisting essentially of a composite of chromium and at least one chromium carbide taken from the class consisting of  $Cr_{23}C_6$ ;  $Cr_7C_3$  and  $Cr_3C_2$  wherein the composite coating contains from 0.2 wt. percent to about 5.4 wt. percent Carbon and the composite is characterized by a multilayer structure of overlapping thin,

lenticular particles, each particle containing a mixture of said chromium and chromium carbides.

8. Article according to Claim 7 wherein the carbon content is in the range of 0.8–1.7 wt. percent.

9. A coated trochoid surface of a rotary combustion engine comprising a metallic surface having a coating thereon consisting essentially of a composite of chromium and at least one chromium carbide taken from the class consisting of  $Cr_{23}C_6$ ;  $Cr_7C_3$  and  $Cr_3C_2$  wherein the composite coating contains from 0.2 wt. percent to about 5.4 wt. percent Carbon and the composite is characterized by a multilayer structure of over-lapping thin, lenticular particles, each particle containing a mixture of said chromium and chromium carbides.

10. A coated trochoid surface of a rotary combustion engine according to Claim 9 wherein the carbon content is in the range of 0.8–1.7 wt. percent.

11. A coated trochoid surface of a rotary combustion engine according to Claim 9 wherein the carbon content is about 1 wt. percent.

12. An article consisting of a composite of chromium and at least one chromium carbide taken from the class consisting of  $Cr_{23}C_6$ ;  $Cr_7C_3$  and  $Cr_3C_2$  wherein the composite contains from 0.2 wt. percent to about 5.4 wt. percent carbon and the composite is characterized by a multilayer structure of over-lapping thin, lenticular particles, each particle containing a mixture of said chromium and chromium carbides.

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