

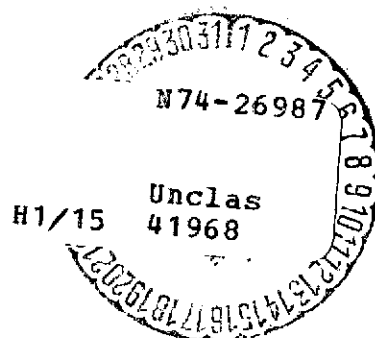
NASA TECHNICAL NOTE



NASA TN D-7688

NASA TN D-7688

(NASA-TN-D-7688) EFFECT OF CHLORINE
PURIFICATION ON OXIDATION RESISTANCE OF
SOME MECHANICAL CARBONS (NASA) 12 p HC
\$3.00 14 CSCL 11D



**EFFECT OF CHLORINE PURIFICATION
ON OXIDATION RESISTANCE OF
SOME MECHANICAL CARBONS**

by Donald W. Wisander and Gordon P. Allen

Lewis Research Center

Cleveland, Ohio 44135



1. Report No. NASA TN D-7688	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle EFFECT OF CHLORINE PURIFICATION ON OXIDATION. RESISTANCE OF SOME MECHANICAL CARBONS		5. Report Date June 1974	6. Performing Organization Code
		8. Performing Organization Report No. E-7809	10. Work Unit No. 501-24
7. Author(s) Donald W. Wisander and Gordon P. Allen		11. Contract or Grant No.	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		13. Type of Report and Period Covered Technical Note	
		14. Sponsoring Agency Code	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		15. Supplementary Notes	
16. Abstract Oxidation experiments were conducted with some experimental and commercial mechanical carbons at 650 ^o C in dry air flowing at 28 cc/sec (STP). In general, purification of these carbon-graphites with chlorine at 2800 ^o C improved oxidation resistance. Additional improvements in oxidation resistance were obtained from purification followed by an anti-oxidant (zinc phosphate) treatment. For the commercial materials, purification alone gave greater oxidation resistance than the antioxidant treatment alone. The reverse, however, was the case for the experimental materials.			
17. Key Words (Suggested by Author(s)) Oxidation resistance; carbon; graphite; purification; inhibitors; seal materials; additives; antioxidants; boron carbide; zinc phosphate; mechanical carbons		18. Distribution Statement Unclassified - unlimited Category 15	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 14	22. Price* \$3.00

* For sale by the National Technical Information Service, Springfield, Virginia 22151

EFFECT OF CHLORINE PURIFICATION ON OXIDATION

RESISTANCE OF SOME MECHANICAL CARBONS

by Donald W. Wisander and Gordon P. Allen

Lewis Research Center

SUMMARY

Experiments were conducted on some commercial and experimental carbon-graphites to determine the effect of purification (with chlorine at 2800^o C) on oxidation resistance. Results are presented for specimens at 650^o C in dry (100 ppm H₂O) air flowing at 28 cubic centimeters per second STP.

The materials used in this investigation were selected from a previous oxidation study. Two of the three experimental materials were boronated (B₄C containing) carbon-graphites. All materials were studied without and with antioxidant (zinc phosphate) treatment ('phosphated') after purification.

The commercial materials showed an improvement in oxidation resistance due to purification. Also the nonboronated experimental material showed an increase in oxidation resistance, but the boronated materials showed no significant increase. (However, even without an increase, the boronated material had the longest life.)

In general, impregnation with zinc phosphate ('phosphating') improved oxidation resistance of the purified and unpurified materials.

In general, purification before phosphating provided an improvement in oxidation resistance.

INTRODUCTION

Advanced aircraft turbine engines require dynamic shaft seals to operate in air at temperatures up to 650^o C. Mechanical carbons have advantages over other seal materials at high temperatures; these are high strength to mass ratios, very high sublimation temperature (>3500^o C) and low elastic moduli (conformability to mating surfaces). The only major disadvantage is relatively poor oxidation resistance.

One factor that affects the oxidation resistance (of carbon-graphites) is the catalytic effect of impurities. In general, commercial materials contain appreciable amounts of

impurities as indicated by ash contents of over 1 percent in extreme cases (ref. 1). Reference 2 indicates that the oxidation rate of carbon is increased by most elements found as impurities.

The purpose of this investigation was to determine the effect of purification on the oxidation life (time to lose weight equivalent to 0.05 cc from 6.45 cm² of surface) of some commercial and experimental mechanical carbons. Most of the materials investigated were selected from a previous study (ref. 3) in which oxidation resistance had been shown to be improved by inclusion of B₄C and by subsequent zinc phosphate treatment.

Results are presented for materials oxidized at 650° C in air flowing at 28 cubic centimeters per second STP (standard temperature and pressure).

APPARATUS AND PROCEDURE

The specimens used were hemispherically tipped cylinders (friction specimens) (fig. 1). The nominal hemisphere and cylinder radii were the same, 0.475 centimeter, and the nominal length was 1.9 centimeters. A hole was drilled near the base of the hemisphere to admit a Chromel wire hook.

The volume and apparent (or geometrical) surface area was determined. After purification and/or phosphating, the specimens were submerged in n-heptane (ASTM reference fuel) and subjected to ultrasonic cleaning to remove loose material and contaminants. They were then evacuated (20 to 30 torr) for at least 36 hours. High-purity nitrogen was used to repressurize the vacuum chamber. The specimens were weighed just before use.

A schematic of the oxidation apparatus is shown in figure 1. Specimen weight was continuously measured with a recording microbalance. The specimen was heated by an induction heated susceptor located in a 5-centimeter-diameter pyrex tube. Specimen temperature was monitored with an infrared pyrometer. The pyrometer emissivity setting was 0.85, established by thermocouple measurement on a carbon-graphite specimen. This emissivity is in the range expected for a rough graphite surface (ref. 4). The error due to incorrect estimate of emissivity is probably low since varying the emissivity setting by 0.05 changes the indicated temperature by 7° at 650° C. The pyrometer output was electrically coupled to a temperature controller which maintained the specimen temperature within an indicated maximum deviation of 10° C.

Specimens were suspended from one arm of the microbalance by a preoxidized Chromel wire. The size and shape of the holes appeared to be unchanged indicating no catalytic effect from the wire. The test envelope was purged with high purity nitrogen gas until the test temperature was reached. The nitrogen flow was then replaced by

clean, dry (to about 100 ppm water) air flowing at 28 cubic centimeters per second (STP). The dry (room temperature) air was directed to the induction heated specimen. Previous observations indicated that the major oxidation loss occurs in the pores; the air temperature has a negligible effect on oxidation. Those specimens for which the mean cylinder radius was remeasured after testing showed no apparent loss from the geometrical surface. Oxidation was continued until about 5 percent of the specimen weight was lost. The time required to lose a weight equivalent to 0.05 cubic centimeter ($\rho \times 0.05$ cc) was determined for each specimen. This time was multiplied by the ratio apparent surface area (sq cm)/6.45 to give an oxidation life that is a normalized 5 percent loss.

MATERIALS

The commercial carbon-graphite materials, designated A and B, were mechanical base grades which, according to the manufacturers, contain no antioxidant or other additives. Some properties are presented in table I.

The experimental materials (prefix E) are part of a series reported in reference 3. Properties of these materials are also presented in table I. These materials contain 30 pph of particulates plus 70 pph of binder (no. 30 medium hard pitch). The particulates consist of 80 pbw CHP graphite, 20 pbw thermax and 0, 5, or 7.5 pbw B_4C (the 0, 5, or 7.5 in the designation). The materials designated EP were impregnated with additional pitch (see step 8 under Base Material Processing). The numbers 22 and 28 denote the graphitization temperatures (2200° and 2800° C) of the compacts.

Base Material Processing

The following outline describes the processing of the experimental materials (More detailed information is available in ref. 5.):

- (1) Blend particulates except B_4C .
- (2) Preheat particulates in mixer, add pitch (binder), and mix (basic E-mix).
- (3) Pelletize the mix, then cool.
- (4) Micromill the mix.
- (5a) For nonboronated materials, blend the milled mix.
- (5b) For boronated materials, preblend half and half B_4C and E-mix, add the remaining required E-mix and blend, screen, and reblend.
- (6) Mold blended material at 150° C and 345 N/cm² (green compact).
- (7) Pack green compacts with coke, cover with charcoal, and bake. Heat rapidly to 50° C; heat at $2\frac{1}{2}^{\circ}$ C per hour to 500° C then at 5° C per hour to 1000° C, and hold

for 4 hours (carbonized compact).

(8) Impregnate with pitch if desired (EP materials) at 70 N/cm^2 . Heat at 5° C per hour to 1000° C and hold 4 hours.

(9) Pack the carbonized compacts (from step 7 or 8) with graphite and heat to the graphitization temperature indicated for each material. Heat at 400° C per hour to 900° C ; 200° C per hour to 1600° C ; 300° C per hour to final temperature and hold for 1 hour.

Purification Treatment

The purification was a commercial process. Specimens were heated to 2800° C in a chlorine atmosphere and held at temperature for $1/2$ hour. During this treatment, impurities are converted to chlorides which are vaporized and removed. Reference 1 indicates that graphite does not react with chlorine.

Antioxidant Treatment

The antioxidant treatment done on some of the specimens can be considered to deposit zinc phosphate. Details are as follows:

(1) Carbon specimens are placed in a closed stainless-steel container, evacuated to 15 to 20 torr, then heated to 800° C , and held at temperature for 60 minutes.

(2) The container, still evacuated, was allowed to cool to room temperature.

(3) The container was backfilled (by suction) with a 25 percent aqueous solution of zinc phosphate. The solution included enough phosphoric acid to give a zinc oxide to phosphorous pentoxide ratio of 1 to 3.

(4) The container was pressurized to 35 newtons per square centimeter with nitrogen and held for 60 minutes.

(5) After depressurization, the specimens were removed and oven dried for about 24 hours at 175° C .

RESULTS AND DISCUSSION

The results presented are median values based on two or three specimens for a given set of variables (material, purification, antioxidant). The specimens of each material were fabricated from a single batch of material. This minimized the variations which usually occur in the manufacture of carbon-base materials. Oxidation life is the

time required to lose 5 weight percent of a 1 cubic centimeter specimen with a 6.45 square centimeter apparent surface area.

Effect of Purification

The effect of purification on oxidation resistance (or life) is presented in figure 2. For the commercial materials (A and B), purification increases the relative life several (5 and 10) times as compared to the unpurified materials. For experimental material E-0-28 (nonboronated), the relative increase of three times was less than for the commercial materials. It should be noted, however, that the oxidation life of unpurified E-0-28 was greater than that of either unpurified commercial material. Also purified E-0-28 falls between the purified commercial materials in oxidation life. These results indicate that the commercial materials contain substantially more impurities than the experimental material. Therefore the superiority of untreated E-0-28 can be attributed to higher purity.

In an earlier study (ref. 3), boron carbide (B_4C) as a constituent of the basic mix was shown to increase the oxidation resistance of carbon-graphite. The effect of purification on two B_4C containing materials is also shown in figure 2. Purification of the experimental boronated materials did not increase oxidation resistance. This lack of improvement is attributed to loss of B_4C during purification. During the work reported in reference 3, weight gains attributed to oxidation of B_4C (to $B_2O_3 + CO_2$) were observed. In this study, however, no weight gains were observed for the purified materials. Therefore, at least the B_4C at and near the surfaces must have been removed during purification.

Effect of "Phosphating" on Purified and Unpurified Materials

Loss of oxidation inhibitor can occur during purification (as with the boronated materials previously mentioned). This is not a problem when the inhibitor (e. g., zinc phosphate) is added after purification. Treatment with zinc phosphate ("phosphating") increases oxidation life of unpurified carbon-graphites (ref. 3). It is desirable to determine how purification followed by "phosphating" compares with purification alone and with "phosphating" alone.

The effects of "phosphating" on purified and unpurified materials are shown in figure 3. In all cases except the unboronated experimental material (E-0-28), there are significant increases in oxidation resistance. As can be seen, the commercial materials (A and B) again show the greatest relative increases ($\times 10$ and $\times 7$). The boronated materials (EP-5-22 and EP-7.5-22), despite loss of B_4C during purification, show an ulti-

mate benefit from purification when "phosphated." And "phosphated" E-0-28 shows very nearly the same life when purified as when unpurified.

Figure 4 gives an overall comparison of the results. For each material, there are two variables - purification and phosphate treatment.

The maximum oxidation resistance was produced by a combination of purification and "phosphating." However, for E-0-28, the difference between "phosphating" alone and the combination of treatments was slight.

For unpurified material A, "phosphating" increased life two times. However (for material A), purification followed by "phosphating" increased life four times. Thus, for material A, purification doubled the increase in life obtained from "phosphating." Similar increases in the benefits of "phosphating" were also observed with EP-5-22 ($\times 2$ unpurified against $\times 5$ purified) and EP-7.5-22 ($< \times 2$ unpurified against $\times 4$ purified).

For the commercial materials (A and B), it is plain that purification alone is superior to "phosphating" alone. The specimens with purification alone averaged somewhat more than twice the life of the specimens with "phosphating" alone for both materials. For the experimental materials, however, it can be seen that "phosphating" alone is superior to purification alone. The reason for this difference between commercial and experimental materials is considered to be due to the difference in material purity.

SUMMARY OF RESULTS

Studies of the oxidation lives of limited numbers of specimens of several commercial and experimental mechanical carbons (carbon graphites) indicated the following results:

1. Purification by a chlorine process increased the oxidation resistance of non-boronated experimental and commercial carbon-base materials. Purification did not increase the oxidation resistance of the boronated materials.
2. Purification followed by phosphate treatment gave the highest oxidation life for each material. But for the nonboronated experimental material phosphate treatment alone gave very nearly the same life as the combination of treatments.
3. For the commercial materials studied, purification alone was superior to the phosphate treatment alone. For the experimental materials, phosphate treatment alone was superior to purification alone.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 7, 1974,
501-24.

REFERENCES

1. Mantell, Charles L.: Carbon and Graphite Handbook. Interscience Publishers, 1968.
2. Maahs, Howard G.; and Schryer, David R.: Chemical Impurity Data on Selected Artificial Graphites with Comments on the Catalytic Effect of Impurities on Oxidation Rate. NASA TN D-4212, 1967.
3. Allen, Gordon P.; and Wisander, Donald W.: Oxidation Resistance of Selected Mechanical Carbons at 650⁰ C in Dry Flowing Air. NASA TN D-7381, 1973.
4. Walker, P. L., ed.: Chemistry and Physics of Carbon. Vol. 3. Marcel Dekker, Inc., 1968.
5. Fechter, N. J.; and Petronich, P. S.: Development of Seal Ring Carbon-Graphite Materials (Tasks VIII, IV, and X). Union Carbide Corp. (NASA CR-121092), Jan. 1973.

TABLE I. - PROPERTIES OF MATERIALS USED IN THIS INVESTIGATION

Material	Average flex strength		Average Young's modulus		Average hardness Rockwell, S	Nominal density, g/cc	Source
	N/m ²	psi	N/m ²	psi			
A	7.7×10 ⁶	11 500	2.0×10 ⁹	2.8×10 ⁶	90	1.85	Manufacturer's literature
B	6.1	8 800	2.6	3.7	---	1.77	Manufacturer's literature
E-0-28	2.63	3 810	1.20	1.74	106	1.83	Ref. 5
EP-5-22	3.83	5 560	1.68	2.44	112	1.86	Ref. 5
EP-7.5-22	4.13	5 990	1.77	2.5	109	1.85	Ref. 5

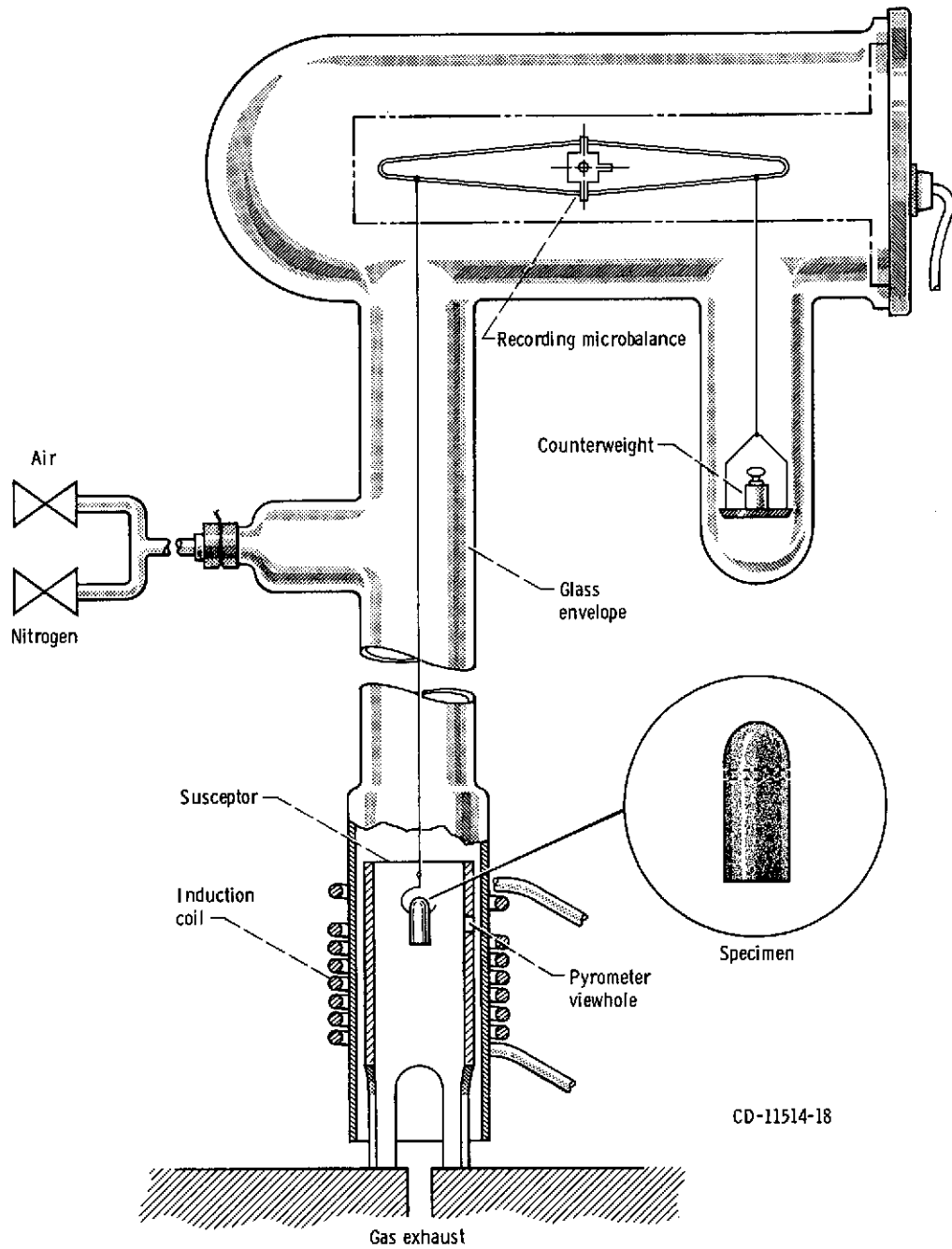


Figure 1. - Schematic of oxidation apparatus.

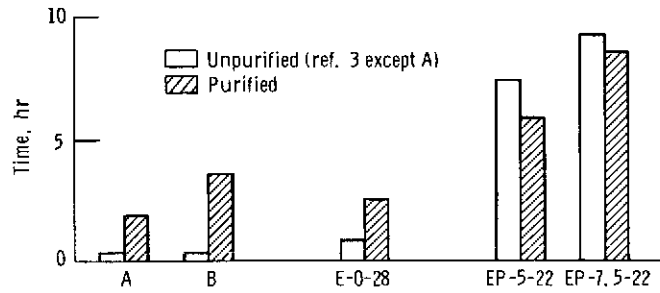


Figure 2. - Effect of purification on oxidation resistance of carbon-graphite materials. Time to lose weight equivalent to 0.05 cubic centimeter from 6.45 square centimeter surface at 650° C.

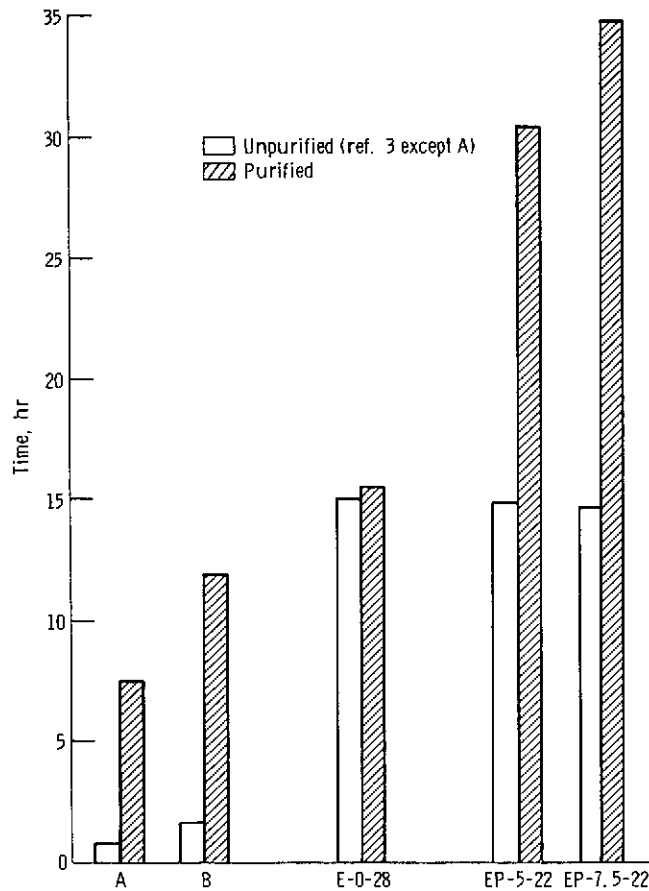


Figure 3. - Effect of purification on oxidation resistance of carbon-graphite materials subsequently treated with antioxidant (zinc phosphate). Time to lose weight equivalent to 0.05 cubic centimeter from 6.45 square centimeter surface at 650° C.

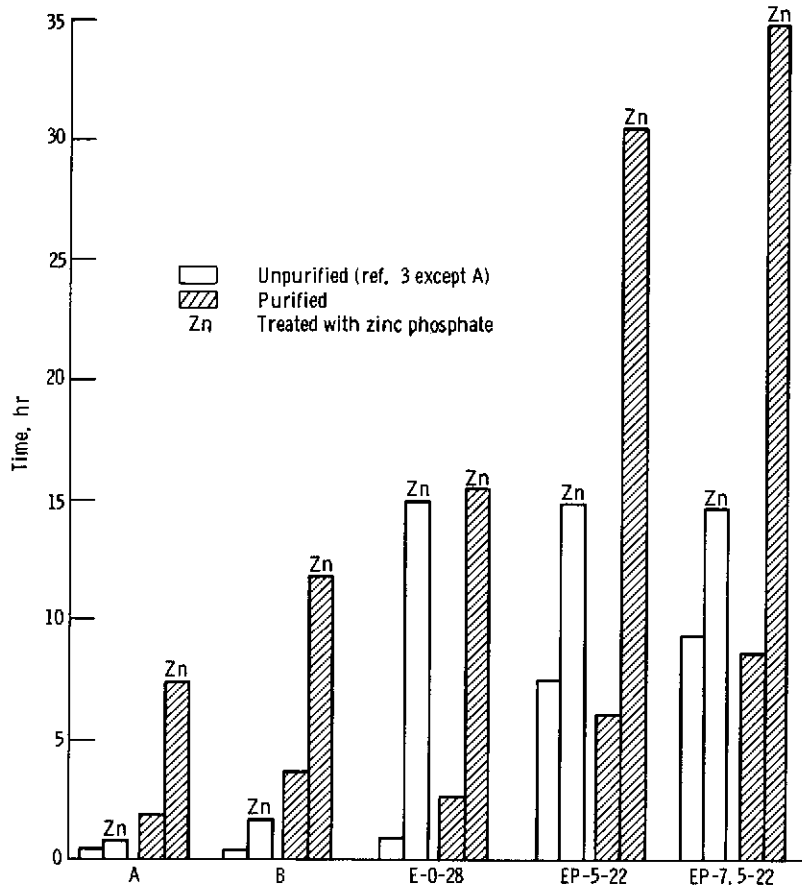


Figure 4. - Effect of purification on oxidation resistance of carbon-graphite materials without and with antioxidant (zinc phosphate). Time to lose weight equivalent to 0.05 cubic centimeter from 6.45 square centimeter surface at 650° C.