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VAPOR PHASE IMPREGNATION OF ACTIVE CARBONS

Quarterly Progress Report No. 1

January Through March 1969

D. Marshall Andrews
John P. Redmond

April 1969

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Physical Research Laboratory
Edgewood Arsenal, Maryland 21010

Contract DAAI5-69-C-0302

COMMONWEALTH SCIENTIFIC CORPORATION
500 Pendleton Street
Alexandria, Virginia 22314

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Project 1B662706A095

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FOREWORD

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SUMMARY

The purpose of this program is to study methods for the vapor deposition of metals and metal salts into the pores of activated carbons, and evaluate properties imparted to the carbons for toxic gas removal by this method of impregnation.

Work in the first phase of this program. part of which is covered by this report, is concerned with copper and chromium vapor phase impregnation studies.

A successful method for the vapor deposition of copper within the carbon pores using copper acetylacetonate as the reactant was developed and samples containing 8%, 4%, 2% and 1/2% copper by weight were prepared using PCC grade CWS carbon. Tests were run on these samples to determine their characteristics.

A technique was developed for the vapor impregnation of activated carbon with chromium trioxide through the ammonolysis or hydrolysis of chromyl chloride which had previously been adsorbed on the carbon. Samples were prepared by this method on carbons which had already been impregnated with copper. Analytical tests performed on the samples showed that chromium was present on the carbon in the +6 oxidation state and copper in the +2 state. The emission spectrograph analysis indicated the metals were present in the predicted concentration range.

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VAPOR IMPREGNATION OF ACTIVE CARBONS

INTRODUCTION

The usefulness of activated carbon as a detoxifying agent because of its relatively high absorption capacity is well known. Activated carbons, however, retain the toxic gases primarily by physical adsorption, and desorption results in recontamination of the air by the toxic compound. Efforts to correct this resulted in the impregnation of carbons with various metals and metal salts which have the ability to catalyze the decomposition or rearrangement of the toxic species into a less toxic material.

Generally, impregnation with metals and metal salts is achieved by a liquid process wherein the carbon is immersed in a water solution containing salts of the catalytic species. Subsequent drying of the carbon results in deposition of the catalyst on the carbon surface. This method does not allow for the full utilization of the carbon, since deposition occurs only in those pores into which the impregnating solution can penetrate.

This program is aimed at optimizing the catalytic activity of impregnated carbons by depositing a thin, uniform film of catalyst over the entire area of the carbon by a vapor deposition process. Essentially, this process consists of passing a volatile compound containing the desired metal into the pores of the carbon and subsequently decomposing the reactant by various means to deposit the catalyst. This technique should result in a finely divided, uniform and highly active catalyst.

APPROACH

During the first quarter, work was focused on the deposition of copper and chrome by vapor impregnation methods to produce a carbon having CK activity equal to or better than ASC whetlerite. At Edgewood Arsenal previous work with ASC carbons showed that copper is most likely present in the catalyst as cupric oxide, and chrome is present in the +6 state.[1] Those processes were studied which deposited the metals either in this form, or in a form which could be easily converted to the proper one. For the deposition of copper, the metal-organic copper acetylacetonate was chosen. This material has been the subject of patents for vapor plating copper.[2] The compound has a melting point of about 230°C and decomposes into copper and acetylacetone above 240°C. Although this process deposites copper as the metal, subsequent treatments with oxidizers converts it to the necessary oxide.

Three methods were chosen for the deposition of chromium. The metal can be deposited from dicumene chromium, a metal organic which decomposes above 300°C to yield chromium and cumene.[3] The chromium can be oxidized to the +6 state by subsequent treatments. The second method consists of vacuum sublimation of CrO_3 into the pores of the carbon. For the third method, chromyl chloride is vaporized under vacuum and adsorbed into the carbon. Controlled hydrolysis of the compound then produces CrO_3 and HCL.

SAMPLE TESTING

Carbons prepared under this program will be subjected to three types of tests to determine their respective properties. These include analytical tests, surface area and pore size measurements and detoxification tests. Results of these tests are not complete as of this writing, and will be reported later.

Analytical Tests

Simple qualitative analytical tests are used to determine the presence of the catalysts on the carbon. These would comprise the following tests:

1. Treat the impregnated carbon with NH_4OH - a deep blue solution indicates +2 copper.

2. Treat NH_4OH extract with lead nitrate - yellow ppt. indicates +6 chrome.

In addition, emission spectrographic analysis are used semi-quantitatively to determine the amount of catalyst present, and X-ray diffraction studies are being made to determine the molecular composition of the catalyst.

Surface Area Tests

The effect of the catalyst on the total surface area of the carbon will be determined from nitrogen adsorption isotherms using the standard BET data plot.[3] Calculation of pore-size distribution will be made from these data using the procedure devised by Cranston.[4] These calculations will aid in determining catalyst uniformity and penetration. The scanning electron microscope will be used also to view the coating inside the pores of the carbon.

Detoxification Tests

Samples of impregnated carbons will be submitted to Edgewood Arsenal for testing of activity against toxic agents. Test with CK (CNCL) will determine the effectiveness of copper and chrome vapor impregnated carbons as compared to ASC whetlerites Evaluation with PS (CCL_3NO_3) will indicate any drop in carbon surface activity brought about by vapor impregnation.

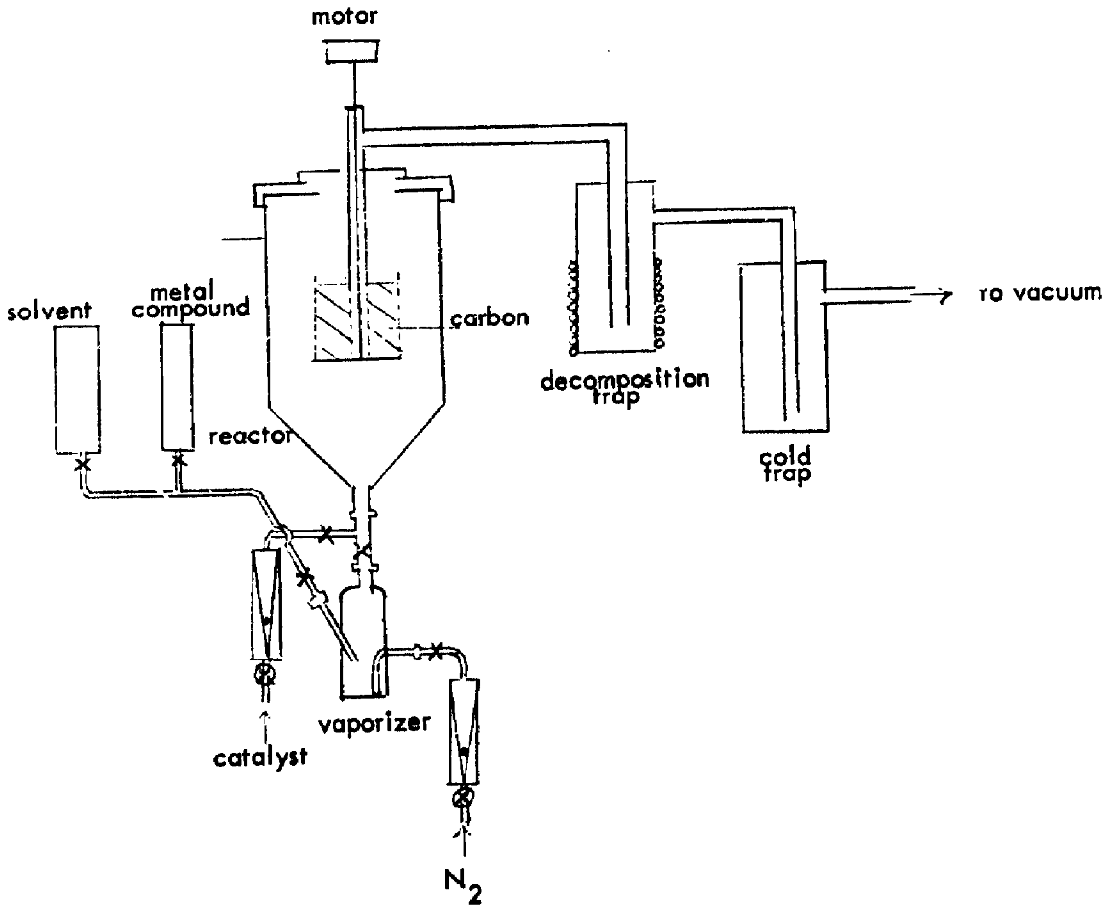
COPPER IMPREGNATION

Most vapor deposition processes are basically the same unit operations, therefore, a system was designed which could be used for several of the processes planned in this program. [See fig. 1]. Carbon placed in the basket is heated by resistance or induction, and continually mixed by the rotating action of the basket. The metal containing compound is vaporized into the reactor where it must pass through the carbon to exhaust. A heated decomposition chamber and a dry ice cold trap prevent harmful exhaust gases from entering the vacuum pump. Measured amounts of catalyst may be introduced into the system in order to induce decomposition.

Several difficulties appeared in the first copper impregnation runs made with copper acetylacetonate. Although the system performed well for the most part, the small temperature range between vaporization and decomposition of this compound caused large amounts to decompose without ever leaving the vaporizer. Most of the material which did vaporize, then condensed out on the reactor walls even though these walls were heated. These experiments did show however, that carbon has a strong affinity for copper acetylacetonate, since the small amount which did reach the carbon was readily adsorbed.

In order to take advantage of this affinity, it was decided to dry mix the carbon and the copper acetylacetonate (CuAA) and heat the mixture under vacuum. This procedure would minimize the distance a molecule of CuAA vapor must travel before contacting the carbon, and thus reduce the possibility of its decomposing or condensing elsewhere. The first runs using this procedure proved to be successful. At a temperature of about 70°C and a pressure of 150u, all of the CuAA has been adsorbed into the carbon as evidenced by the disappearance of the blue colored CuAA. Decomposition of the organo-metallic begins at a carbon temperature of about 100°C with a pressure of 150u. The rate of decomposition continues to increase without any loss of reactant up to about 200°C and 350u. At these conditions, the occurence of sublimation out of the carbon is evidence by condensation of material on the cool neck of the reaction flask.

FIGURE 1



GENERAL VAPOR DEPOSITION APPARATUS

Several runs made using this method, resulted in the following procedure for vapor impregnating carbon with copper from CuAA.

I Outgas Carbon

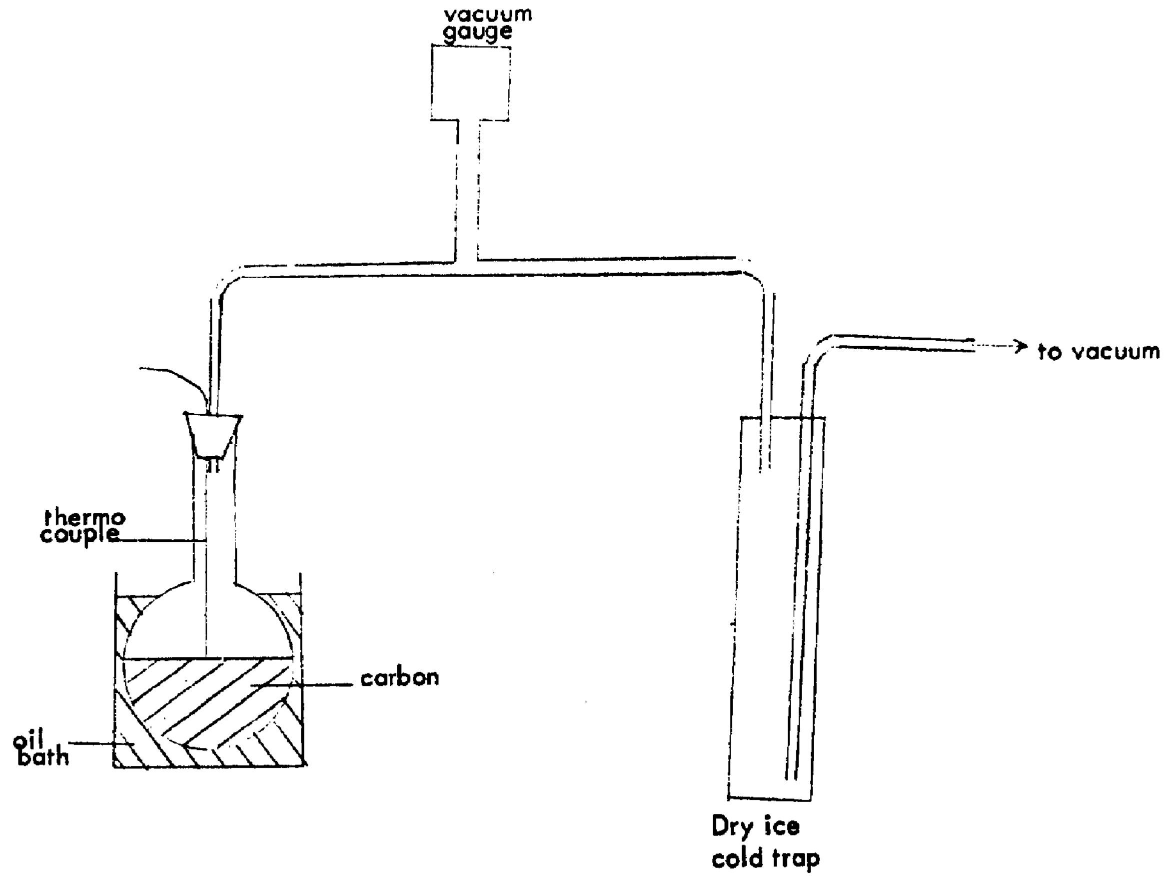
(a) weigh into a round bottom flask of known tare the quantity of carbon to be impregnated (not to exceed 1/2 the volumn of the flask).
(b) connect the flask to the vacuum system [Fig. 2] and begin evacuating
(c) turn on oil bath. Heat and set control for 300°C
(d) keep a record of temperature and pressure variations
(e) when pressure is less than 250u for a carbon temperature of 275°C, turn off heat
(f) when carbon temperature drops below 150°C, return system to atmospheric pressure
(g) reweigh carbon and determine weight loss

II Impregnate Carbon

(a) to the flask containing the carbon from Part I, add the amount of CuAA to give the desired weight percent of copper [CuAA is 24.3% Cu by weight] therefore, it requires four times the weight of CuAA to obtain a given weight percent Cu, i.e., for a 100 gm sample of carbon add 16 gm CuAA to get a 4% by wt copper impregnation
(b) Shake the flask to intimately mix the carbon and CuAA
(c) connect flask to vacuum system [Same as Fig. 2] and begin pump down
(d) when pressure drops below 500u, turn on heat and set for 100°C
(e) keep a record of T & P variations
(f) after carbon has reached 100°C and all of the CuAA has been adsorbed, set temperature for 180°C
(g) keep carbon temperature between 180° and 190°C until pressure drops, indicating decomposition is almost complete; then set temperature for 275°C to finish the reaction.
(h) when pressure begins to drop at 275°C, turn off heat and allow carbon to cool down below 100°C
(i) restore system to atmospheric pressure and weigh carbon

From the initial carbon weight, final carbon weight and weight of CuAA used, the percentage completeness of the decomposition reaction can be calculated. If the above procedures are followed, the reaction will be better than 90% complete, and very little CuAA will be lost through sublimation. Because the rate of decomposition is rather slow below 200°C, however, this procedure requires a relatively long reaction time. A 150 gm sample of carbon to be impregnated 4% by wt with copper required about 7 hrs by this method. Time requirements can be reduced considerably by ignoring step 2 and raising the temperature up to 275°C, however, as much as 20% of the CuAA will be lost through sublimation.

FIGURE II



COPPER DEPOSITION APPARATUS

CrO_3 IMPREGNATION

As a result of difficulties involved in oxidizing chrome from the metal to the +6 state, it was decided to postpone examination of deposition processes involving dicumene chromium in favor of the more direct chromyl chloride vaporization and CrO_3 sublimation methods. Even with chromyl chloride, a hydrolysis step is necessary to produce the +6 oxide, thus initial experiments were performed using CrO_3.

Experience with copper impregnation from CuAA had taught that materials with low vapor pressure such as CrO_3 must be brought in close initial contact if vapor impregnation is to be achieved. As a result dry CrO_3 was mixed with outgassed carbon in the same manner as CuAA for copper impregnation, [See Fig. 2] a vacuum drawn, and the material heated. Several runs were made using this method with each run having a different ultimate sublimation temperature [Table 1]. Analysis of the carbon after each run showed in all cases that little or no chromium had been adsorbed by the carbon. Pressure rises noticed above 150°C during impregnation indicated also that reduction of the CrO_3 which did adsorb on the carbon was occuring, with the production of CO_2. These results showed that CrO_3, unlike CuAA, has little or no tendency to adsorb on carbon. Carbon samples were impregnated with ammonia and water in an attempt to increase the affinity of carbon for CrO_3. Samples for this run were tested for CrO_3 by treating them with water to dissolve off any CrO_3 and adding lead nitrate. Only a small amount of yellow ppt. was seen, indicating that very little CrO_3 had been adsorbed. This combined with the low vapor pressure of CrO_3 and its ease of reduction to Cr_2O_3 at elevated temperatures, ruled out vacuum sublimation as a method of vapor impregnating carbon with CrO_3.

The next method tried involved the use of chromyl chloride CrO_2Cl_2, a dark red liquid, which boils at 117°C. This material may be converted to CrO_3 by water or any other compound capable of replacing the chlorine in chromyl chloride with oxygen.

The first experiment with chromyl chloride consisted of vaporizing the material under vacuum, into copper impregnated carbon placed in a glass tube. This run showed that carbon has a strong affinity for CrO_2Cl_2 as a large amount of the compound was adsorbed by the carbon, and heat was generated during the adsorption. Having saturated the carbon with CrO_2Cl_2, water vapor was passed through in order to hydrolyze the CrO_2Cl_2 to CrO_3. Once again heat was generated. Analytical tests performed on the material from this experiment indicated that some of the chrome had been reduced to the +3 state, and some of the copper had been converted to $CuCl_2$.

In order to prevent the unwanted conversion of CuO to $CuCl_2$, NH_4OH was tried as a means of tying up the chlorine. Runs made by this ammonolysis treatment also yielded heat and showed some reduction of chromium to the +3 state, however, no $CuCl_2$ was detected. Finally, an ice water bath was used to reduce the heat generated during the

TABLE I EXPERIMENTAL PARAMETERS FOR VAPOR IMPREGNATION OF CARBONS

RUN NO.	METAL COMPOUND	SYSTEM FIGURE NO.	CARBON TEMP °C	REACTANT	DEP. PRESSURE MILLIMETERS	WT %	RESULTS
1	CuAA	1	330	--	2	--	CuAA decomposed in vaporizer & condensed on reactor walls.
2	CuAA	1	260	--	0.25	--	Heated walls & lower pressure failed to prevent condensation of CuAA.
3	CuAA	2	260	--	0.5	8	Analytical tests showed presence of Cu although most CuAA remained unreacted.
4	CuAA	2	300	--	0.3	8	Higher final temp & longer reaction time produced 75% conversion of CuAA to Cu.
5	CuAA	2	275	--	0.3	7	Used final proceedure for CuAA conversion, reacted 90% complete.
6	CrO_3	2	180	--	0.2	-	Only a small amount of CrO_3 found on carbon
7	CrO_3	2	200	--	0.08	-	Same as 6 with some +3 chrome found
8 (a)	CrO_2Cl_2	Straight Tube	80	H_2O	5	-	Some +3 chrome & some $CuCl_2$ most Cr & Cu on carbon in water insoluble form.
8 (b)	CrO_2Cl_2	Straight Tube	80	NH_4OH	5	-	Some +3 chrome - no $CuCl_2$
9	CrO_2Cl_2	Straight Tube	60	NH_4OH	1	2	Slow addition of reactants keep down heat & formed little +3 Cr.
10	CuAA	2	275	--	0.3	4	Sample sent to Edgewood Arsenal (EA) 94% conversion.
11	CuAA	Straight Tube	60	NH_4OH	Atmos.	-	Carbon from run #5 saturated with NH_4OH for Cr dep. runs 12 & 13.
12	CrO_3	2	155	Carbon from Run 11	0.2	2	Analytical tests showed little Cr on carbon. Sample sent to EA.
13	CrO_2Cl_2	3	150	Carbon from Run 11	0.4	2	Used final procedure for Cr dep. Sent sample to EA.
14	CuAA	2	275	--	0.3	2	95% conversion. Sample sent to EA.
15	CuAA	2	275	--	0.3	1/2	95% conversion. Sample sent to EA.

reaction from getting excessive. Tests made on samples from this run showed no reduction of +6 chrome, and no formation of $CuCl_2$.

From these results, the following method for the deposition of CrO_3 was adopted:

(a) Place previously copper impregnated carbon into flask shown in Fig. 3 and evacuate.

(b) When pressure drops below 500u close valve A and open valve B to allow NH_4OH, or any other compound capable of exchanging an oxygen atom for the chlorine atoms, to enter the reaction flask and impregnate the carbon.

(c) When impregnation is complete (about 3 minutes), close valve B and open valve A to sweep out excess reactant.

(d) When pressure drops below 1000u, close valve A and open valve C to allow CrO_2Cl_2 to enter flask and impregnate carbon.

(e) When the amount of chromyl chloride necessary to give the desired wt. % of CrO_3 has been vaporized, close valve C and open valve A to remove products.

(f) After the pressure drops below 1000u, close valve A and open valve B to complete the conversion.

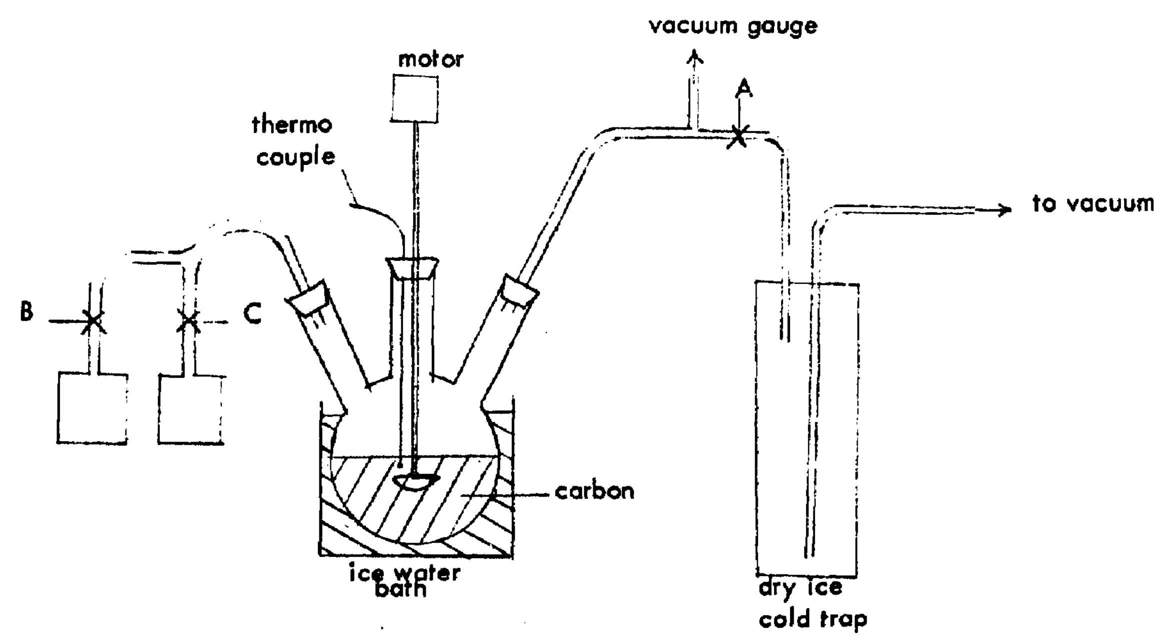
(g) When reaction is complete (about 3 min) remove ice water bath, close valve B and open valve A. When pressure drops below 500u shut off pump and restore system to atmospheric pressure.

PREPARATION AND TESTING

Analytical test performed on samples prepared by the above mentioned vapor impregnation procedures showed that these procedures deposited copper and chrome on carbon in the desired form and with high efficiency. Therefore, nitrogen adsorption isotherm were performed on samples of untreated carbon and samples from runs #5 and #13 to determine changes in surface area of the carbon caused by the impregnation. These test showed that an 8% by wt copper impregnation causes a 15% reduction in surface area from 1125 sq. m/pgm the untreated carbon, to 452 sq m/gm for the impregnated sample. Adsorption isotherms for samples from run #13 indicated that 2% CrO_3 impregnation along with the 8% copper lowers the surface area another 17% to 764 sq m/gm.

Samples from runs #12 and #13, containing copper and CrO_3, were sent to Edgewood for CK and PS break through testing. In all cases, the vapor impregnated samples showed shorter break through time than the untreated carbon. Tests with chloropicrin (PS) which is removed by physical adsorption rather than catalyzed decomposition, showed a 32% reduction in wt percent adsorbed. This is consistent with the fact that there was also a 32% reduction in surface area, as calculated from nitrogen adsorption isotherms by the BET equation for the vapor impregnated samples. As a result, samples from run #10, a 4% by wt copper impregnation,

FIGURE III



CHROMIUM DEPOSITION APPARATUS

were tested for PS break through times. These samples showed times equal to that of untreated carbon, indicating an insignificant drop in surface area with this degree of loading.

CONCLUSIONS AND RECOMMENDATIONS

Vapor impregnation methods can be used to deposit catalysts within the pores of activated carbons. Results of nitrogen adsorption isotherms and PS break through tests on 8% by wt Cu impregnate indicates, however, that considerable reduction in surface area is produced by this high loading. The 4% by wt impregnate does not show this loss of surface area, therefore, this concentration will be used for future impregnation.

Although analytical tests indicate that copper and chrome are present on the vapor impregnated carbon in the same oxidation states as on the ASC whetlerite, CK break through tests showed no significant catalytic activity for the vapor impregnated sample. Future work in this phase will be devoted to varying the catalyst deposition and activation procedures in order to produce impregnated carbons with CK activity.

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*Bed Area is 2.93 cm^2.

APPENDIX

EDGEWOOD ARSENAL BREAKTHROUGH TIME TESTS FOR VARIOUS IMPREGNATED CARBONS

Sample No.	Date	Inlet Conc. mg/L	Volume Flow L/min.	Linear Velocity cm/min	Carbon Volume cm^3	Carbon Weight g	Relative Humidity	Temp °F	Protective Life Min. As is	Protective Life Min. corrected	Bed Depth cm.	Gas
Control 8425C PCC	3/12/69	4.12	1.675	575	15	6.10	80	80	5.6	5.77	5.2	CK
8425C PCC	3/12/69	4.12	1.675	575	15	5.91	80	80	5.5	5.66	5.2	CK
8425C PCC	3/12/69	4.08	1.675	575	30	11.40	80	80	23.2	24.6	9.9	CK
8425C PCC	3/12/69	4.27	1.675	575	30	12.3	80	80	24.7	25.2	11.0	CK
8425C PCC	3/12/69	4.08	1.675	575	7.5	2.73	80	80	1.5	1.5	2.4	CK
8425C PCC	3/12/69	4.08	1.675	575	7.5	2.72	80	80	1.5	1.5	2.4	CK
8425C PCC	3/12/69	4.08	1.675	575	22.5	9.56	80	80	14.4	14.63	8.4	CK
8425C PCC	3/12/69	4.08	1.675	575	22.5	8.87	80	80	12.2	12.67	8.5	CK
II- 12 - 3/5 P-I (8)Cu(3)Cr	3/18/69	4.28	1.68	575	10.0	5.22	80	84	1.7	1.8	3.9	CK
II- 12 - 3/5 P-I (8)Cu(3)Cr	3/18/69	4.28	1.68	575	10.0	4.65	80	84	1.9	2.0	3.9	CK
II- 12 - 3/5 P-I (8)Cu(3)Cr	3/18/69	49.88	1.07	365	10.0	5.37	0	-	32.0	32.1	3.6	PS
II- 13 - 3/6 P-I (8)Cu (2)Cr	3/18/69	4.28	1.68	575	10.0	5.24	80	84	1.1	1.18	4.0	CK
II- 13 - 3/6 P-I (8) Cu(2)Cr	3/20/69	4.28	1.68	575	10.0	4.85	80	84	1.0	1.07	3.9	CK
Control 8425C PCC	3/20/69	49.88	1.07	365	10.0	3.76	0	-	36.4	39.2	3.4	PS
Control 8425C PCC	3/20/69	49.88	1.07	365	10.0	2.51	0	-	17.2	19.5	2.3	PS

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Vapor Phase						
Active carbons						
Metals						
Metal salts						
Toxic gas removal						
Copper disposition						
CWS carbon						
Ammonolysis						
Hydrolysis						
Chromyl chloride						
Spectrographic analysis						

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