U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio 45226

HEALTH HAZARD EVALUATION DETERMINATION REPORT
HE 78-7-666

KAWECKI BERYLCO INDUSTRIES, INC.
BOYERTOWN, PENNSYLVANIA

February 1980

I. SUMMARY

At the request of Locals 619 and 959 of the International Chemical Workers Union, the National Institute for Occupational Safety and Health (NIOSH) conducted a health hazard evaluation at Kawecki Berylco Industries, Inc. in Boyertown, Pennsylvania, in January and February of 1978, and again in April of 1979. The purpose of the visits was to evaluate the basis for complaints by the titanium diboride process workers over possible health effects from exposure to carbon black, especially the possibility that the carbon black might contain polynuclear aeromatic carcinogens.

The on-site investigation took place in two phases: the initial investigation in January and February of 1978, and a follow-up visit in April of 1979. The follow-up visit was necessitated by changes in the size, methods, and number of workers involved in the process being investigated, as well as changes in the NIOSH criteria for determining hazardous exposure to carbon black.

Confidential medical interviews were conducted and bulk, area, and personal breathing zones samples were collected and analyzed. Carbon black in use, both during the initial and follow-up visits, was found to contain well above 0.1% cyclohexane - extractable fraction, the level required to be classified as PNA contaminated carbon black. Analyses for five specific PNA's were negative at the limits of detection for the method used. There are however, so many other potentially carcinogenic PNA's that it is not possible to test for each one individually.

On the basis of the data obtained in this investigation, NIOSH determined that a potential hazard of exposure to carbon black containing polynuclear aeromatics existed at Kawecki Berylco Industries, Inc. Therefore, all exposure to this substance must be carefully controlled and monitored. Recommendations for improved controls are contained in the body of this report under the section "Conclusions and Recommendations."

II. INTRODUCTION/BACKGROUND

Under the Occupational Safety and Health Act of 1970* the National Institute for Occupational Safety and Health investigates the toxic effects of substance found in the workplace. NIOSH received such a request from employees representing two locals of the International Chemical Workers Union #619 for the production workers and #959 for the laboratory workers. The request involved exposures to the Titanium Diboride (TiB_2) production process. Primary concern was expressed over exposure to carbon black which could be contaminated with Polynuclear Aromatic Hydrocarbons. Three visits were made during two different operating modes. Publication of the NIOSH carbon black criteria subsequent to the second visit necessitated the third set of environmental measurements. The process had undergone substantial alterations in operation, equipment, and facilities during the interim. The process had progressed from a three man intermittent pilot plant operation in two facilities to a one man continuous production operation in one facility. This report provides additional and updated information that was previously discussed during the closing conferences following the initial January 1978 visit and in our SHEFS I Interim Report of August 8, 1978, which reported the data, included herein, from the January and February 1978 visits.

III. METHODS AND MATERIALS

A. Process Description

The KBI plant at Boyertown processes a wide variety of products. The plant employs around 375 workers, 140 of which are production workers and 42 of which are Research and Development (R&D) technicians. Each group is represented by a separate union local.

1. Initial Survey

At the time of the January and February 1978 initial survey eight people were qualified TiB_2 operators. They worked two per shift with a supervisor in the process area and a third worker operating the fine grinder.

The process includes blending titanium dioxide (TiO_2), boron carbide (B_4C) and carbon black to formulate a batch charge for a vacuumed sintering furnace. After the heating and cooling period the product titanium diboride (TiB_2) was processed physically by jaw crushing, screening, ball milling, and fine grinding.

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*Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

This process was in a developmental phase when the HHE request was generated. The R&D methods had been converted to a pilot production operation at the time of the initial survey in early 1978. The process was run on an intermittent basis as sales demanded, typically every few months. During the January 1978 visit only the fine grinding was in operation. It was located in a separate building. During the follow-up visit in February 1978 the workers assigned to the process were laboratory R&D technicians who were not following the previously established production procedures. The process cycle was about six days. The technician was instructed on each step of the batch process. This was reportedly due to some production problems encountered by production personnel using the established procedure. The operation observed was similar to that conducted previously by R&D personnel with variations as reported.

During the initial visits individual process activities were separated by sufficient time that each activity was observed independently. The initial blending activity was followed by oven drying. The furnace was loaded by hand scoop and the product sintered. After a weekend cool down period the furnace was unloaded by hand scoop. The furnace walls were cleaned by scraping and brushing. Waste was picked up by a portable vacuum cleaner. Respirators were used when it was dusty. The primary contact with carbon black occurred during the formulating and blending activity when hand weighing and frequent intermitten additions of water to the blender is required. Following furnace unloading the product was run through a jaw crusher located adjacent to the furnace platform. The only local exhaust was a vacuum cleaner hose hung above the crack at the top of the fines collection box drawer. When ball milling was initiated the jaw crusher was still in operation. Finally the ball mill outputs were passed through an air-vibrated screening to proper size. Those passing were either used as is or sent to another building for fine grinding. The fine grinder was very noisy and in need of constant attention due to its poor operating condition. The operator did wear a respirator and ear defenders when working at the fine grinder. Hoses and connections were leaking TiB_2 dust. Tape was used to reduce losses. It was a dusty operation.

2. Follow-up Survey

In April of 1979, there were two production operators and a supervisor. One operator per shift, working two 8-hour shifts except on days when furnace runs were made, then 12-hour shifts were required typically twice per week.

The production process and facilities observed on the final visit in April 1979, were substantially altered from those previously observed. The old fine grinder had been replaced by a new fine grinder which was installed in the primary TiB_2-process building. The process had been running at continuous production for several months. The large jaw crusher had replaced the smaller laboratory model and a local exhaust dust collection system was installed on it. Additional blending equipment had been installed and the physical arrangement had been substantially altered. In addition, the processing had been modified to eliminate a ball milling activity and automate a courser screening step.

During the April 1979 visit the separation of activities was not always possible. In a full production mode several activities are normally being conducted simultaneously. We were fortunate to come at a time when the cycle was interrupted. The formulation blending activity on the evening shift of April 3 was conducted without any other sources of contamination operating. They were very similar to those observed in February 1978. Similarly the furnace unloading and loading of the furnace in the a.m. on April 4 was without any interfering activity. This procedure was altered from the previously observed activity in two ways. The respirators available for use previously offered only particulate protection. Operators were now using SO_2 cartridges in addition to dust masks. The loading was previously done by hand scoop. However, this time the drum was lifted by hoist and poured into the carbon furnace. The cleanup was by vacuuming as before however, the vacuum discharge was outside rather than through portable cloth bag system used previously. The furnace was scraped to remove deposits and, as before, the deposits ignited when brushed from the surface. There was a lot of smoke, dust, and strong sulfur odor.

The afternoon portion of the April 4 day shift involved the combined exposures of jaw crushing, dry blending, and fine grinding operations. The operator also started a ball mill operation on TiB_2, but it was halted since production does not normally require this procedure now that the new fine grinder has been installed. The ball milling of another substance, Tantalum Carbide (TaC), was completed during this shift and it was screened. This facility had been used previously to manufacture TaC; however, there was none being produced at that time. The handling of fine products causes a higher level of dust exposure during jaw crushing, dry blending, and fine grinding. The fine grinder generates even finer dust when material is run through twice. This is generally controlled by a bag collection ventilation system. The fine grinder dust exposures occur when filling and checking the grinder and when emptying the grinder collector into a plastic bag after the run. During the night shift of April 4 an added exposure occurred when the air compressor was shut down causing an accumulation of fines in the fine grinder cabinet. The jaw crusher operator receives exposures during crushing and when filling and emptying the dry blender. This activity on the night shift was in conjunction with formulation blending. No furnace run was possible since the vacuum pump failed and was down for repairs. Therefore the shift was not extended to 12 hours. This resulted in a shorter sampling period for both the day and night shift than would have normally been expected.

The jaw crushing operation takes about 1.5 to 2 hours to process a drum if there are not too many interruptions. The new fine grinder requires 7 to 9 hours of operation per batch. After the startup the fine grinding cabinet side doors are opened about every 15 minutes to check the flow and material is added to the top hopper every hour.

The jaw crusher ventilation system design did not make most effective use of the collection systems capabilities. The two branch ducts each had two 90° angles. The hoods over the receiving buckets were open slots with no baffling. They would be much more effective with covers extending over part or all of the top of the buckets.

3. General Ventilation

The general ventilation was unchanged between visits, however, it was undoubtedly somewhat more effective since two sets of double doors one on each side of the building, were left partially open during most of the follow-up survey. In the winter this is not possible. The general ventilation in the process building consisted of one large (36 inch) axial exhaust fan located in the buildings outer wall adjacent to the formulating blender platform at the work level. The other fan was located in the interior wall at ceiling height above the furnace platform. Interior fan air is discharged above the furnace power pannel and air pump equipment at the opposite end of the room where crushing, ball milling, and dry blending activities are now located. The exhaust fan was operated during the February survey when the formulating activity was underway. There are space heaters for temperature control. The interior fan was run during furnace cleaning and loading/unloading activities in February. During the April 1979 survey these fans both operated during the whole shift with outer double doors partially open. Operation of the interior fan resulted in a recirculation of air from the furnace room entering through personnel doors on the furnace platform and the opposite end of the room through the blending area double door. Smoke tube observation showed a rapid movement of air high above the furnace platform, however, little movement below ten feet above the platform.

B. Evaluation Design

Area samples were collected in three locations on each survey. They were taken during each shift to show comparative exposures from various activities throughout the buildings. The personal breathing zone samples were collected on an operator and a fine grinder operator during the initial survey and on the single operator during the final survey. A different sampling method was used on the follow-up survey to obtain better carbon black data and to evaluate airborne cyclohexane solubles. Bulk samples of carbon black were taken for determination of PNA contamination. During the final survey a bulk rafter sample was analyzed for PNA content and a bulk sample of furnace wall deposit was given qualitative analysis. Seven of the eight TiB_2 workers in January 1978 and both of the workers in April 1979 were given confidential medical interviews.

Observations of work practices, respirator usage, and general ventilation were made. Early pilot production was observed on the initial survey and full production was observed on the following survey although some deviations from normal operations were present during both surveys as noted in the report.

C. Evaluation Method

1. Initial Survey

Personal breathing zone samples were collected side by side, one total dust sample and one respirable dust sample on opposite lapels. They were collected with MSA model G pumps operating at 1.7 LPM and closed face cassettes containing 2.0u polyvinyl chloride filters. A nylon cyclone preceded the respirable filter.

Area samples were collected in pairs similar to the above but using a Gast pump with two 9 LPM limiting orifices and a 1/2 inch stainless steel cyclone.

Analytical methods and limits of detection are as follows: Gravimetric and titanium analyses of the first eight samples collected on 2u filters during fine grinding on January 8, 1978, were by equilibration method and P&CAM 178 method respectively. The gravimetric analysis accuracy of measurement is ±20 ug. In the atomic absorption method P&CAM 173 spiked filters were run concurrently with the samples. The average recovery was 91.5%. The relative standard deviation (RSD) for the analytical portion of the method is 2%.

Gravimetric analysis of samples taken in February was again by equilibration. Four of the more heavily loaded filters in the 1.9 to 3.1 mg/filter range were selected for qualitative analyses by X-ray powder diffraction from $20\text{-}52^{\circ}2\Theta$.

2. Follow-up Survey

Personal breathing zone samples were collected side by side, one total dust and carbon black and one cyclohexane soluable sample on opposite lapels. They were collected with DuPont 2000 P pumps operating at 2.0 LPM and closed face cassettes.

Total dust samples, which were ashed for carbon black, were collected on 0.8u 37 mm acrylonitrile polyvinyl chloride copolymer DM800 filters during the final survey. Samples for cyclohexane-solubles and PNA's were collected on a glass fiber silver membrane filter combination.

Area samples were collected in pairs similar to the above but using a Gast pump with two 9 LPM limiting orifices.

Gravimetric and low temperature ashing were accomplished on the April 1979 dust samples. Preweighed DM800 filters were reweighed after sample collection to determine total weight gain on each filter. Each filter was then placed in a preweighed aluminium pan and placed in the LFE Low Temperature Asher (LTA) to ash the carbon black and other organics. The samples were ashed under vacuum using radio frequency power and oxygen. The temperature reached is approximately 70°C.

When ashing was complete, each aluminium pan was weighed. The weight loss on each pan is considered to be the maximum possible amount of carbon black contained on the filter.

Cyclohexane soluables analysis were accomplished by NIOSH method P&CAM 217 limits of detection is 0.02 mg/sample.

3. Bulk Samples

Bulk samples of carbon black taken in January 1978 and April 1979 were analyzed for cyclohexane solubles by NIOSH method #217. The limit of detection is 0.02 mg per sample.

The remainder of the extract was further analyzed for Polynuclear Aromatic Hydrocarbons (PNA) by reverse-phase high pressure liquid chromatography utilizing a Waters Associates HPLC System equipped with a Vydac 201TP column running a methanol/water solvent gradient. Retention times of specific peaks in the chromatograms were compared with those of known standards for analytic identification. Quantitative data were obtained by comparison of peak areas with standards curves. Limits of detection (see table below) for the two sample sets were slightly different since the January 1978 set was run with 50 ul injections while the April 1979 set was run with 40 ul injections. Also, the bulk sample volumes varied.

	January 1978	April 1979
Fluoranthene	0.02 ug/sample	0.037 ug/sample
Pyrene	0.10 ug/sample	0.12 ug/sample
Chrysene	0.06 ug/sample	0.05 ug/sample
Benzo(a)anthracene	0.02 ug/sample	0.05 ug/sample
Benzo(a)pyrene	0.02 ug/sample	0.025 ug/sample

Personal samples were not analyzed for the PNA's since the bulk samples did not show them to be present in the carbon black. Only the cyclohexane soluble fraction was run on them. The bulk carbon black and rafter samples were also submitted to low temperature ashing.

Bulk sample #3, scrapings from the furnace vessel wall, was submitted to qualitative analysis by X-ray diffraction from 8 to 96 degrees 2θ and to X-ray fluorescence for 76 elements above fluorine. The data from XRF and XRD were subjected to computer analysis and matching with standard reference tables.

IV. Evaluation Criteria

1. Carbon Black

In 1965 the Threshold Limit Value (TLV) for occupational exposure to airborne concentrations of carbon black was recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) to be limited to a Time Weighted Average (TWA) 8 hour per day 5 day per week exposure of 3.5 mg/M^3. OSHA has adopted this standard. NIOSH published a criteria for a Recommended Standard --- Occupational Exposure to Carbon Black in September of 1978.[2] NIOSH recommended that Polynuclear Aromatic (PNA)* contaminated carbon black be controlled by a different criteria. Contaminated carbon black was defined as that which contained 0.1% cyclohexane soluble fraction in bulk sample analysis. The airborne exposure to the contaminated carbon black is determined by measuring the cyclohexane soluble fraction of personal breathing zone samples. This should not exceed a 10-hour day 40-hour work week TWA exposure of 0.1 mg/M^3 cyclohexane solubles. Since the cyclohexane soluble fraction is considered to be a potential human carcinogen these criteria are to be considered the upper boundary of exposure and every effort should be made to keep the exposure as low as feasible.

The health effects of carbon black:[2] Based on a review of toxicologic and epidemiologic studies, there is evidence to suggest that carbon black may cause adverse pulmonary and heart changes. Carbon black also has the capability of adsorbing various PAH's, which may pose a cancer risk. Also skin effects have been reported after persons had contact with carbon black. However, the available toxicologic and epidemiologic information has deficiencies. Therefore, further scientific research is needed to confirm the pulmonary, heart, and skin changes attributed to carbon black exposure. The cancer risk from carbon black exposure should also be more clearly defined.

Although carbon black by itself has not been shown to cause cancer, various studies have shown that PAH's are adsorbed on carbon black.[2] The desorption of adsorbed PAH's may occur under various conditions. Such desorption may occur in work environments with elevated temperatures or solvent vapors. The PAH's may be eluted from carbon black by human blood plasma and under certain health conditions, such as acute respiratory infections.

*PNA's may also be referred to as Polycyclic Aromatic Hydrocarbons (PAH's).

The basis of the recommended carbon black criteria is as follows:

a. Since there is inadequate information available to associate carbon black exposure concentrations of 3.5 mg/M^3 with an effect that can be directly attributed to carbon black this limit should be maintained pending further investigations.

b. The differentiation between PAH-containing carbon black as that containing 0.1% cyclohexane extractables is based on professional judgement, rather than on data delineating safe from unsafe conditions of PAH's. This limit results in an maximum airborne concentration of PAH's of 0.035 mg/M^3 when the carbon black is at its proposed limit of 3.5 mg/M^3. This is significantly lower than 0.1 mg/M^3 which was justified on the basis of feasibility of measurement, not on its safety.

c. The rationale in choosing the 0.1 mg/M^3 TWA limit for cyclohexane extractables is chiefly based on the fact that with today's personal monitoring methods it is the least concentration reliably detectable. The selection of cyclohexane-extractable materials, rather than analysis of one or more specific compounds is based on the argument presented in References 3, 4 and 5. As reviewed in these documents PAH's contain many substances often thought or known to be carcinogenic. In addition there are factors affecting tumor yields and carcinogenic responces, including either enhancement or inhibitation of carcinogenesis by compounds within the same class of chemicals. The concentration of specific compounds in any sample of PAH's are variable.

2. Nuisance Dust

The ACGIH TLV for nuisance dust is 10 mg/M^3 TWA total dust or 5 mg/M^3 respirable dust. At these levels the worker is protected from seriously reduced visibility, unpleasant deposits in the eyes, ears, and nasal passages, and from injury to the skin or mucous membranes by chemical or mechanical action or by the rigorous skin cleansing procedures necessary for their removal. This criteria is not used for exposures to substances which might cause organic disease, toxic effects, or scar tissue to be formed in lungs. Nuisance dust inhalation has the following lung tissue reaction characteristics:

a. The architecture of the air spaces remain in tact
b. Scar tissue is not formed to a significant extent
c. The tissue reaction is potentially reversible

3. Titanium Dioxide, Titanium Diboride, and Boron Carbide

Titanium dioxide, boron carbide, and titanium diboride are currently considered to be nuisance particulates. However, there has been some questions raised about the fibrogenic and liver toxicity potential of titanium diboride and boron carbide. A study by I.T. Brakhnove[6,7] reported these effects on animals from the intratracheal administered dose of 50 mg. A NIOSH toxicologist considered this dose to be excessive, and the number of doses was not explicitly stated. The doses would more appropriately have been 1, 5 and 10 mg to permit a valid assessment of the toxicological properties of such a material. Doses in excess of 10 mg may cause onset of respiratory diseases and 50 mg doses overwhelm the mechanisms of the lung and quite often yield false positive responses which are not evident at more realistic physiologic doses. The lack of dose - response data in animals and any evidence of health impairment in man, coupled with scientific knowledge on substances similar to titanium diboride and boron carbide, suggests that these materials are more appropriately classified at this time as nuisance particulates rather than fibrogenic dusts.

V. FINDINGS AND DISCUSSION

Bulk Sample Analysis

The bulk carbon black sample analysis results for percent cyclohexane extractables and PNA's are shown in table 1. This data shows a range of cyclohexane content from 4.3 to 16.5 mg/g. Therefore all of the carbon black bulk samples exceeded the 0.1% criteria. Carbon black samples designated B-2A, 2B, and 2C of the product currently in use ranged from .4% to 1.6% cyclohexane extractables. The bulk rafter sample taken from the formulation blending area was found to contain 1.6% cyclohexane extractables. None of the samples contained detectable quantities of BaP, BaA, Fluoranthene, Pyrene, or Chrysene which are the routinely tested for PNA known or suspect carcinogens. There are of course a large number of other PNA's which are potential carcinogens.

Both career black samples collected on the follow-up survey were totally ashed when subjected to LTA leaving no measurable ash residue. The bulk rafter sample lost only 2.7 mg of the 10/mg initial weight.

The XRF analysis of furnace lining scrapings for seventy-six elements above fluorine indicated the presence of sodium, silicon, phosphorous, sulfur, potassium, titanium, and lead. The XRD analysis indicated some amorphous material. The X-ray diffractogram reveled only two large peaks from which no identification of a compound can be made.

Initial Survey Airborne Contamination Measurements

The results of total dust and respirable dust samples taken in January and February 1978 are shown in table 2 along with the X-ray defraction and titanium analyses. Airborne exposure levels during formulation and mixing are the most likely to include carbon black. Respirable personal breathing zone data ranged from 0.38 mg/M^3 to 1.7 mg/M^3. Total personal breathing zone data was from 0.43 mg/M^3 to 1.5 mg/M^3. They are well below the OSHA Standard of 3.5 mg/M^3 for total carbon black. The dust levels during jaw crushing and ball milling operations ranged from 0.35 mg/M^3 respirable to 60 mg/M^3 total. This is in excess of the current OSHA total dust standard of 15 mg/M^3 for nuisance dusts as well as the American Conference of Governmental Industrial Hygienists (ACGIH) criteria of 10 mg/M^3. Fine grinding operations were observed on January 12 and February 23 the total personal breathing zone dust measurements were 20 mg/M^3 and 37.5 mg/M^3, respectively. These results show a need for improved ventilation controls in the jaw crushing, ball milling and fine grinding operations. With the exception of an infrequent ball milling/screening operation non of these activities are presently operating the same way they were then.

It can be seen by comparison of the total dust and respirable dust sample pairs that there is a relatively small respirable dust fraction with the possible exception of the formulating/mixing operation.

The qualitative analysis by X-ray defraction and the quantitative titanium analysis show a significant portion of the total dust is titanium oxide and titanium diboride with a lesser amount of tantalum carbide. It also shows that furnace emptying exposures include titanium, silicon, calcium, and iron.

Follow-up Survey Airborne Contaminant Measurements

The cyclohexane soluble fraction of airborne dust exceeded the 0.1 mg/M^3 criteria during the morning loading and unloading activities at 0.19 mg/M^3. The TWA for the 7 1/2 hour survey period was between 0.11 mg/M^3 and 0.09 mg/M^3. Therefore it is considered a marginal exposure. The total dust exposure was also the highest on this shift with a TWA of 16.8 mg/M^3 for the 7 1/2 hour sample period. The Low Temperature Ashable fraction was also the highest observed with a 4.8 mg/M^3 during the furnace activity and 1.29 mg/M^3 during the crushing and fine grinding activity for a TWA of 2.93 mg/M^3. The 4.8 mg/M^3 ashable fraction would probably include a significant contribution from the furnace wall deposit dust. There would also be a possibility that this material might contribute to the cyclohexane soluable fraction. Although the qualitative XRF/XRD analysis identified elements, it is not possible to state that no organics were present. The very high temperature 2000°C oven environment would minimize the presence of PNA's in the furnace deposits.

The formulating and blending activity was remarkably low in total dust (2.57 mg/M^3) during the 6.75 hour April 3 activity when no other sources were operating. The cyclohexane fraction was measured at 0.07 mg/M^3 for the first 4 1/2 hour exposure during the dustiest activities. The Low Temperature Ashable fraction was only 0.54 mg/M^3 for the same period. This shows a significant contrast to the April 4 night shift exposure data which included the formulating and blending activity in conjunction with fine grinding activity. The total dust was 8.14 mg/M^3 for the 6.2 hour sample period. Notably the cyclohexane extractables were $<$ 0.03 mg/M^3 for this period, however, the maximum carbon black was 2.48 mg/M^3. During this period there was no furnace cleaning activity to consider in these results. Had this exposure continued at this level through a 12 hour shift, which is the normal work period during furnace operation, it would be considered in excess of the adjusted 2.3 mg/M^3 carbon black TLV for the extended work shift.

Controls And Work Practices

The dusty conditions were recognized prior to this survey. A new fine grinder was on order at that time and was in operation during the April survey. Further improvements were made by installing local ventilation over the large jaw crusher receiving buckets. The local exhaust hoods design and branch duct angles are not making efficient use of the collection system. Considerable visible dust is generated by the jaw crusher even with the local exhaust system in use. The fines which pass a #5 screen are dumped into one of the two newly installed dry blenders. There is a large visible dust cloud each time the bucket is dumped. The fine grinder is operated simultaneously with frequent checks by the same operator and addition of feed material to the hopper once an hour. The wood fine grinder enclosure is typically left open on top and sides for ease of access and to facilitate electric shop light cards. The deposits of dust in the cabinet show another potential source of contamination. From observation of the past and present fine grinding activities, it is evident that the new installation is a great improvement. However, the new fine grinder process is located in building 5 and is now in the same work area and operated by the single operator therefore it is a contributor to his overall dust exposure. The furnace loading and unloading has been slightly altered to reduce dust exposure. The loading by dumping the drum instead of a scoop at a time is much faster and requires less worker contact. The use of an remote vacuum bag system is much preferable to the portable cloth bag vacuum used previously for clean up after furnace unloading, cleaning, and loading activities.

There was an obvious effort underway to improve the respirator program. Operators on both shifts were given mask fit tests on April 4. There was still some confusion over the proper respirator usage storage. The operator during oven cleaning used a Wilson AR700 respirator and R25 cartridge (approval TC-23C-76) approved for use with organic vapors, chlorine, sulfur dioxide, and hydrocarbons. The marking on the box in which they were stored was R-12 TC-21C-142 approved for dust, fumes, and mists. These were the type of cartridges previously used. Workers now wear the chemical cartridge mask when opening and cleaning the furnace. They used the NORTON dust respirator model 7170 (approval TC-21C-170) during dusty operations such as formulating and other activities as the worker deemed appropriate. The use of "PNA contaminated" carbon black requires a continuing effort to control exposures both through engineering and where necessary personal protection. The frequent opening and hand scraping of the blender when adding water to the formulation blender is one possibility for process modification. There are reportedly some modifications being studied which could eliminate this type of operator exposure through automation.

Confidential Interviews

Nine workers with experience in TiB_2 operations were interviewed, seven in January 1978 and two in April 1979. The 1978 interviews of intermittently exposed workers included five lab technicians and two production workers. In 1979 only two production workers were assigned TiB_2 duties full time. The complaints were generally of dust and odor during the 1978 interviews. Three reported dust masks were not preventing accumulations of dust in their noses. There were four who reported an apparent connection of TiB_2 odors with bowel movements after working in the process. Two of these also had loose bowels. Two complained of difficulity removing dirt from their skin. Cleaning of hands was observed to be a problem. It is very hard to remove carbon black. Workers hands showed deposits of dirt and the skin was cracked pissibly due to defatting from frequent attempts to wash hands.

VI. CONCLUSIONS AND RECOMMENDATIONS

The carbon black used in the process was found to have an excessive content of cyclohexane extractables implying contamination by PNA's. A continuing effort is needed to minimize exposures to the contaminated carbon black. The most effective measure would be to eliminate the contaminants from the process. The apparent variable percent solubles would indicate a need for continuing quality control to assure that the soluble contaminants are less than 0.1% in the raw carbon black materials. NIOSH recommendations for a carbon black standard should be implemented in accordance with reference 2.

In view of the high total dust exposures it is necessary to improve ventilation and/or emission control. From the observations of work activities it is recommended the following measures be implemented:

a. Provide modifications to the large jaw crusher local exhaust system to more effectively capture the dust. The additon of a baffle over all or part of the fine bucket collection point will improve the collection efficiency there. Much less dust is generated at the course bucket collection point. The addition of a third slot pickup drawing air across the top of the feed hopper and away from the operator should be considered. It was noted that the branch duct design for this system incorporates two right angles in each branch. The branch entry losses and elbow losses would be reduced if a 30° and 60° angle were employed thereby increasing the air flow and capture efficiency.

b. There was a visibly heavy dust cloud generated during the pouring of fines from buckets into the dry blenders. This procedure was accomplished with both blender port holes open. The use of a pouring chute sock and/or a filter cap to reduce the dust carried out with displaced air may be helpful. There is a similar dust cloud from pouring the fine grinder processed fines from the collection drum into a plastic bag. The possibility of using a liner in the drum should be explored. This would eliminate the pouring procedure. It should be noted that during the February survey fine grinder fines were considered a potential fire hazard due to heating. This must be given careful study in developing the proper handling procedure and materials.

c. The circulating fan mounted above the furnace platform in the interior wall is not an effective means of emission control for furnace cleaning loading, and unloading activities. The recirculation of these contaminants as well as dust carried back into the furnace room from jaw crushing activities would contribute to the over all dust exposure in the building. It would be more suitable if the fan were exhausted to the outside; however, relying on this general dilution concept is not normally the most efficient solution. Consideration should be given to using a local exhaust hood designed to capture the contaminants at their source. This will require much less air exhaust and therefore less replacement air.

d. Automation of the water blending activity would reduce the workers contact with carbon black. Therefore such a process change is desirable.

e. The use of respiratory protective devices is not considered an acceptable practice for routine exposures where process changes or engineering controls are feasible. They are used as an interim measure until other controls can be implemented or in cases where other means are not feasible or provide incomplete control. The respirator program as outlined in 29 CFR part 1910.134 must be implemented.

f. Hygiene facilities are important because of the worker's frequent hand contact with carbon black. The water is turned off during winter months to avoid freezing of pipes which are above ground. Hot water should be provided for frequent hand washing in this facility. To avoid dermatitis, workers should be instructed on proper use of protective gloves and creams as well as cleaning agents.

g. NIOSH is currently conducting another investigation (HE 79-87) that will assess potential health hazards associated with exposure to boron and carbide compounds at Kawecki Berylco Industries. Therefore, no recommendations concerning medical surveillance will be made at this time.

VII. REFERENCES

1. American Conference of Governmental Industrial Hygienist, Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1978. ACGIH, Cincinnati, Ohio.

2. National Institute for Occupational Safety and Health - Criteria for a Recommended Standard...Occupational Exposure to Carbon Black (NIOSH Publication No. 78-204) U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1978.

3. National Institute for Occupational Safety and Health - Criteria for a Recommended Standard...Occupational Exposure to Coal Tar Products (NIOSH Publication No. 78-107) U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1977.

4. National Institute for Occupational Safety and Health - Criteria for a Recommended Standard...Occupational Exposure to Asphalt Fumes (NIOSH Publication No. 78-106) U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1977.

5. National Institute for Occupational Safety and Health - Criteria for a Recommended Standard...Occupational Exposure to Coke Oven Emmissions (NIOSH Publication TR-003-73) U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1973.

6. Brakhnove, I.T.: Comparative Evaluation of the Effects of Transient Metal Boride and Carbide Dust with Respect to the Features of Their Electron Structure. Gigiena Truda (Russian) 13(1):26-31, 1969.

7. Brakhnove, I.T.: Toxic Effect of Refractory Compounds and Measures for Preventing Occupational Diseases among Workers in Powder Metallurgy Plants. Studies In Soviet Science. Consultants Bureau, New York and London.

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IX. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office at the Cincinnati address.

Copies of this report have been sent to:

a. Plant Manager, Kawecki Berylco Industries
b. Employee Representative, ICW Locals 619 and 959
c. International Chemical Workers Union
d. NIOSH, Region III
e. OSHA, Region III

For the purpose of informing the (10) affected employees, the employer will promptly "post" the Determination Report in a prominent place(s) near where exposed employees work for a period of 30 calendar days.

Table 1

Cyclohexane Extracts from Carbon Black

Kawecki Berylco Industries
Boyerton, Pennsylvania

January 1978, April 1979

Carbon Black Number	Collection Data	Total Cyclohexane Soluble Mg/g	BaP Mg/g	1,2 - Benz-anthracene Mg/g	Fluoranthene Mg/g	Pyrene Mg/g	Chrysene Mg/g
B-1	1/12/78	4.28	<0.01	<0.01	<0.01	<0.02	<0.01
B-2A	1/12/78	4.30	<0.01	<0.01	<0.01	<0.02	<0.01
2B	4/3/79	7.63	<0.01	<0.01	<0.01	<0.02	<0.01
2C	4/4/79	16.23	<0.01	<0.01	<0.01	<0.02	<0.01
B-3	1/12/78	16.48	<0.01	<0.01	<0.01	<0.02	<0.02

Mg/g = milligrams per gram.

TABLE 2

Respirable and Total Dust Samples for TiB_2 Production

Kawecki Berylco Industries
Boyerton, Pennsylvania

January/February 1978

Location	Date (1978)	Sample Type	Sample Period+	Sample Vol M^3	Mg/M^3 Resp	Mg/M^3 Total	XRD++ Major/Minor	%Titanium
Formulating/Mixing Operation	2-22	BZR*	0830 - 1035	.21	.38			
	"	BZT**	" "	.21		1.5		
	"	BZR	1035 - 1320	.28	.93			
	"	BZT	1035 - 1345	.28		1.0		
	"	BZR	1345 - 1445	.10	1.7			
	"	BZT	" "	.10		1.1		
	"	BZT	(5.3 Hr. TWA of above)			1.4		
	"	BZR	(4.9 Hr. TWA of above)		1.0			
(Furnace Platform)	"	AR+++	0840 - 1420	3.06	.34			
	"	AT++++	" "	3.06		.48		
(Mixing Platform)	"	AR	0825 - 1430	3.29	.15			
	"	AT	" "	> 3.29+++		<.54	TiO_2 TaC	
Furnace Loading	2-23	BZR	0815 - 1000	.17	.76			
	"	BZT	" "	.17		3.29		
(Furnace Platform)	"	AR	" "	.94	.51			
	"	AT	" "	.94		.61		
Empty Furnace & Jaw Crushing Operations	2-27	BZR	0815 - 1230	.25	2.32			
		BZT	" "	.25		35.0	Ti, Si, Ca, Fe	
Jaw Crushing & Sieving Operations (on Furnace Platform)		BZR	1330 - 1605	.20	2.1			
		BZT	" "	.20		60.0		
		AR	0815 - 1240	2.1	.83			
		AT	" "	2.1		1.42	TiB_2/TaC	
		AR	1330 - 1605	1.4	.5			
		AT	" "	1.4		1.6	TiB_2/TaC	
Jaw Crushing & Sieving	2-28	BZR	0230 - 0740	.32	2.34			
		BZT	" "	.30		36.9		
Fine Grinding	1-12	BZR	1326 - 1600	.25	.2			32
	"	BZT	" "	.25		20.0		8
(At Operator's Chair)		AR	1242 - 1616	1.92	.21			38
		AT	" "	1.92		.31		42
(At Lounge Table)	"	AR	" "	1.89	.04			<< 1
		AT	" "	1.89		.11		< 1
Fine Grinding	2-23	BZR	0830 - 1315	.40	3.63			
	"	BZT	" "	.40		37.5	TiB_2	
(At Operator's Chair)		AR	0840 - 1215	1.8	1.4			
		AT	" "	>1.8+++		<9.9		

*BZR - Denotes personal breathing zone sample taken at 1.7 lpm (liters per minute) with a cyclone to collect only the respirable fraction.
**BZT - Denotes personal breathing zone sample taken at 1.7 lpm with closed face cassette for total dust.
***AR - Denotes area samples taken at 9 lpm with a ½" cyclone for respirable fraction.
****AT - Denotes area sample taken at 9 lpm with closed face cassette for total dust.
+ - Sampling periods shown may include broken periods when pumps were removed.
++ - XRD Powder X-ray Defraction 20 to 52°, 2θ
+++ - Denotes sample collected at high flow rate >9 lpm exact volume unknown.

TABLE 3

Total Dust/Low Temperature Ash/Cyclohexane Soluble
Kawecki Berylco Industries
Boyerton, Pennsylvania

April 3-4, 1979

Work Task/Location		Cyclohexane Soluble mg/m^3		Total Dust mg/m^3	Max Carbon mg/m^3	SPL Volume M^3	SPL Period Hrs: Min	TWA mg/m^3 Cyclohexane Soluble	TWA mg/m^3 Total Dust	TWA mg/m^3 Max Carbon	(Hrs) Period
(1600-2315 on April 3, 1979) Formulation and Blending	PBZ* GF- 1	0.07	D-30	2.7	0.57	0.54	4:30	<0.07	2.57	0.72	6.75
" " "	PBZ GF- 6	<.07	D-36	2.30	1.19	0.270	2:15				
Blending Platform Area	GF- 2	0.01	D-31	0.27	0.14	2.38	4:25				
" " "	GF- 7	0.05	D-45	0.36	0.28	1.21	2:15				
Jaw Crusher Area	GF- 3	0.03	D-32	0.15	0.12	2.34	4:20				
" " "	GF- 8	0.03	D-41	0.79	0.02	1.21	2:15				
Furnace Platform Area	GF- 4	0.02	D-34	0.21	0.17	2.29	4:15				
" " "	GF- 5	<.02	D-48	0.34	0.26	1.21	2:15				
(0800-1130 on April 4, 1979)											
Unload and Load Furnace	PBZ GF-11	0.19	D-39	17.9	4.8	0.42	3:28				
Furnace Platform Area	GF-13	0.08	D-37	1.5	0.37	1.84	3:25				
Jaw Crusher Area	GF-12	0.02	D-55	0.54	0.44	1.8	3:20				
TiB$_2$ Blender Area	GF-14	<.01	D-73	0.66	0.35	1.8	3:20				
(1200-1600 on April 4, 1979)											
Jaw Crush and Fine Grinding	PBZ GF-18	<.04	D-46	15.8	1.29	0.48	4:00				
Furnace Platform Area	GF-16	0.01	D-40	1.1	0.22	2.13	3:57				
Jaw Crusher Area	GF-15	0.02	D-66	3.0	0.49	2.12	3:56				
TiB$_2$ Dry Blender Area	GF-17	0.01	D-43	12.3	1.64	2.12	3:56				
TWA Breathing Zone for 0800-1600 shift(GF-11 and GF-18) (D-39 and D-46)						.9	7:28	(<.09 <.11)	16.8	2.93	7.5
(1600-2320 on April 4, 1979)											
Formulating Blending and	PBZ GF-23	<.03				GF 0.79	6:25	<.03			GF 6.4
Fine Grinding	PBZ		D-47	8.14	2.48	D 0.74	6:10		8.14	2.48	D 6.2
						GF 3.64	6:45				
Blending Platform Area	GF-24	0.01	D-35	0.7	0.22	D 3.87	7:10				
Jaw Crusher Area	GF-21	0.01	D-52	0.24	0.02	3.94	7:18				
Furnace Platform Area	GF-22	0.02	D-44	0.87	0.06	3.94	7:18				

*PBZ = Personal Breathing Zone.