The Vinyl Institute
A Division of The Society of The Plastics Industry, Inc.

April 30, 1990

TO: VI Health, Safety and Environment Committee

R:E SPI Filing/TSCA Section 8(e)

The enclosed "Report on Encapsulation of Lead Chromate Pigment in Plastic Resins Relative to the Workplace Hazardous Materials Information System (WHMIS) Classification" has been submitted by SPI to the EPA pursuant to the requirements of TSCA Sec. 8(e).

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April 12, 1990

Document Processing Center (TS-790)
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Environmental Protection Agency
401 M Street, SW
Washington, DC 20460

RE: Lead Chromate Pigments in Plastic Resins Relative to WHMIS Classification

Enclosed pursuant to section 8(e) of the Toxic Substances Control Act (TSCA) is a copy of:

> Report on Encapsulation of Lead Chromate Pigment in Plastic Resins Relative to the Workplace Hazardous Materials Information System (WHMIS) Classification

This letter is intended to inform the agency of the findings reported therein. We understand that members of SPI might rely on this letter to satisfy any obligations that they might have to submit this information individually under section 8 (e) of TSCA.

The enclosed report was mailed to members of the SPI (US) Occupational Health and Environmental Issues Committee March 22, 1990. It was also the subject of a presentation to the Committee on April 5, 1990. The report indicates that under the conditions of the test, lead chromate was extracted from plastic resin pellets containing lead chromate pigment.

CTL019156

SPI is a trade organization of more than 2000 members representing all segments of the plastics industry in the United States. SPI's operating units and committees are composed of resin manufacturers, distributors, machinery manufacturers, plastics processors, moldmakers, and other industry-related companies and individuals. Founded in 1937, SPI serves as the "voice" of the plastics industry.

Sincerely,

Hugh Patrick Toner

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Enclosure

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leadchro.epa

REPORT ON

ENCAPSULATION OF

LEAD CHROMATE PIGMENT IN

PLASTIC RESINS RELATIVE TO

THE WORKPLACE HAZARDOUS MATERIALS INFORMATION

SYSTEM (WHMIS) CLASSIFICATION

PRESENTED BY

G.P. ROBSON

ENVIRONMENTAL SCIENCE

DUPONT CANADA INC.

REPORT ON ENCAPSULATION OF LEAD CHROMATE PIGMENT IN PLASTIC RESINS RELATIVE TO WHMIS CLASSIFICATION

INTRODUCTION

The attached report was presented to the SPI Canada Ad Hoc Group of Manufacturers of Concentrates and Compounds on 1990 February 20.

The information contained in the report was developed at the request of the Ad Hoc Group in an attempt to shed light on the WHMIS status of "encapsulated" hazardous ingredients in plastic resin concentrates or compounds, using lead chromate pigment as a model. This was needed to decide whether workers could be exposed to lead pigment during anticipated use of lead chromate-pigmented plastic resins.

The Ad Hoc Group arranged for the manufacture of the pigmented resins, the supply of the regrind materials and data from acid extraction tests. My responsibility has been to arrange for electron microscopy and photon spectroscopy and to interpret the results.

At the February 20 meeting, we all recognized that although the data developed provide an incomplete picture of the overall situation, and there is no will to continue the investigation at this time, they may represent an important change in our understanding of the availability of additives in plastics resins versus the position we have adopted to date.

The Group agreed that the report should be shared with SPI (U.S.) in order to inform them and to solicit their comment and feedback on any implications versus the OSHA Hazard Communication Standard.

* * * *

1990 March 01

ENCAPSULATION OF LEAD CHROMATE PIGMENT IN PLASTIC RESINS AND ITS IMPACT ON WHMIS CLASSIFICATION

SUMMARY

WHMIS regulations in Canada require that untested mixtures be classified according to the toxic properties of ingredients in the mixture. The Plastics Industry considers that it is unreasonable to apply this concept to plastic resin concentrates and compounds which contain toxic ingredients, without regard for the availability of such ingredients to cause worker exposure.

An SPI Canada Ad Hoc Committee of manufacturers of compounds and concentrates proposed that data be developed to provide a better understanding of how toxic ingredients are distributed in plastic resins and their availability to be released and cause worker exposure under anticipated use conditions. Part of that activity involved the preparation and testing of lead chromate pigmented PVC, ABS and PE resins as 3 mm dia. cylindrical pellets. Lead chromate was selected as a "model" substance since it is commonly used and is a WHMIS Controlled Product - as a carcinogen.

Resin pellets were examined by Scanning Electron Microscopy (SEM) and X-Ray Photon Spectroscopy (XPS) to determine whether lead chromate pigment particles were exposed at the pellet surface or were truly encapsulated in the resin. SEM showed that pigment particles were at or close to the surface but due to the slight surface penetration of the electron beam - up to 1 micron - it was not known whether they were actually exposed at the surface. XPS provides quantitative information on elements at surfaces and only penetrates monolayers at the surface approx. 50A. 1 micron is equivalent to 10,000A. XPS showed that the lead pigment concentration at PVC pellet surfaces was similar to the bulk concentration; PE pellets showed traces of lead pigment at the surface. In ABS pellets no lead was detected at the surface since silicate-encapsulated lead chromate pigment was used. Similar XPS results were obtained from fractured pellet surfaces which revealed the interior or bulk composition.

Extraction of whole pellets in 5% aqueous hydrochloric acid for 10 minutes, using a standard test to simulate stomach acid digestion, showed that some lead was extracted in all cases, in approximate proportion to the lead pigment concentration in the resin. The average proportion of lead extracted from whole pellets was 0.08% of the total lead in the resin but the actual levels of lead extracted were below 0.03%. The effect of resin size reduction, eg. as dust, on lead extraction by acid, is not known. Assuming that dust inhalation is the principal workplace exposure route of concern for plastic resins, tests were conducted to measure the inspirable dust concentration (i.e. <100 micron particle size) in commercial reground resin. Samples of ABS, PVC and HDPE commercial regrind resin (not lead chromate pigmented) contained a maximum of 0.002% dust less than 150 microns. Testing of one grade of 5 mm dia. PE resin pellets by rolling in a steel can for one hour to simulate attrition in steel containers or pneumatic conveying lines produced 0.0012% dust less than 177 microns. It is not known how a broad range of plastic resins would rate in evaluating their potential to produce inspirable dust.

Several possible ways of using the 0.1% (or 1.0% as appropriate) minimum concentration for WHMIS classification of mixtures are suggested which could apply to plastic resins. Some discussion will be required to decide on their value and applicability.

Based on these data we should reconsider the use of the term "encapsulated" for additives in plastic resins. It is clear that some lead chromate pigment particles are actually exposed at the surface and are not covered by a layer of plastic resin. I suggest the term "bound" would be more accurate.

INTRODUCTION

The regulation relating to WHMIS Classification and the use of the arbitrary 0.1% or 1.0% by weight ingredients minimum concentrations for classification of untested mixtures for toxicity and corrosivity, involve the inherent assumption that such ingredients are available in a form such that workers can be exposed to them. Also these cut-off concentrations recognize that ingredients present below these concentration values will not be considered in classifying untested mixtures because they will not contribute significantly to the hazards of the mixture.

The concept of hazardous ingredients present in materials to which workers cannot be exposed under anticipated use conditions is the basis for the exclusion of manufactured articles from WHMIS classification. This concept has not been extended so far to cover materials other than manufactured articles.

Commercial thermoplastic resins such as polyethylene, polypropylene, polyvinylchloride, polystyrene, acrylonitrile/butadiene/styrene copolymers (ABS), and acetals, are tough materials which do not shatter easily under impact or grinding conditions to form fine powders, and which are essentially insoluble in water and body fluids.

When such resins contain WHMIS Controlled Product ingredients such as non-volatile pigments, fillers, stabilizers or reinforcing agents (fibres), the ingredients are dispersed in the polymer matrix by melt compounding and when resin compound pellets are produced for commercial use, the ingredients are bound firmly within the pellet and are not available in any significant amount to cause exposure of workers to the ingredients under normal use conditions.

In order to demonstrate experimentally that non-volatile additives are bound in plastic resin matrices, we must recognize the three human exposure routes for plastics resin ingredients, viz: (i) inhalation, (ii) ingestion, and (iii) eye or skin contact/absorption.

Note: Re Scope of Bound Ingredients

Ingredients which are volatile under melt processing conditions to release gases, vapours or aerosols (i.e. small liquid or solid particulates which condense in air from vapour released) are not considered as being bound in the plastic resin. Such ingredients will be subject to the normal WHMIS classification rules for untested mixtures, eg. residual styrene in styrene-based polymers.

The following criteria are proposed for additives which can be considered to be bound in plastic resins:

1. Additive has not significant vapour pressure at worst case melt processing temperatures (what is significant?).

2. Additive has decomposition temperature well above melt processing temperatures.

3. Additive can be well dispersed in the resin, i.e. no large agglomerates exist.

4. Additive does not migrate or diffuse to the surface of resin pellets on storage.

5. Grinding of scrap or reclaim does not liberate the free additive or expose the additive in a way that can cause harm to workers.

Note: In most cases all five conditions should be met. Exceptions may occur, eg. azodicarbonamide blowing agent is a WHMIS controlled product ingredient used in some resins, but is intended to decompose to release nitrogen gas under normal melt processing conditions.

Skin or eye contact is not considered to be a concern provided that the additive does not migrate significantly to the surface of the resin pellet.

For inhalation and ingestion we are concerned primarily with exposure to dust, since pellets will not be ingested or inhaled.

Dust can be generated in several ways:

i) during resin compounding by manufacturer:
   - fines from attrition of pellets during handling, pneumatic conveying and packaging; and
   - dust from grinding of product or grinding of recycle or reject material.

ii) during use by customer;
   - fines from handling and pneumatic conveying; and
   - dust from grinding recycle material.

EXPERIMENTAL WORK

Experiments were carried out:

1. Commercial resin pellets containing lead chromate pigment were examined by electron microscopy, x-ray photon spectroscopy and acid extraction to determine the location and availability of the lead pigment at the pellet surface.

2. Commercial resin pellets containing azodicarbonamide were examined to determine the potential for dust production by attrition and release of the free azodicarbonamide ingredient.

3. Commercial resin regrind samples were examined t determine the amount of fine dust produced.

RESULTS

1. PVC, ABS AND PE RESINS CONTAINING LEAD CHROMATE PIGMENT

a) Scanning Electron Microscopy of Surface of 3 mm dia. x 3 mm long Pellets

Scanning electron microscopy (SEM) of resin pellets was carried out to determine if the lead chromate pigment could be detected at, or near, the surfaces. Some pellets were fractured in liquid nitrogen and the fractured surfaces examined to determine if the interior was significantly different from the external surface. Resins containing 33 to 50% pigment (concentrates) and also 2% pigment (compounds) were examined. Since different sources of concentrate were used to prepare the pellets it was found that ABS resin contained silica-encapsulated lead chromate pigment. PE and PVC resins contained non-encapsulated lead chromate pigment.

The detailed results and copies of the photo-micrographs obtained on the SEM at Queen's University are in Appendix 1. Note that SEM is not a quantitative technique.

In summary the following conclusions were made:

i) Lead pigment particles were detected at or close to the surface in all cases. For PE and ABS the pigment concentration did not appear significantly different between the fractured interior and exterior samples. For PVC there appeared to be a greater pigment concentration at the exterior surface compared to the fractured, internal surface.

ii) SEM showed pigment particles at or close to the pellet surface but, because the electron beam penetrates the resin surface to a depth of up to 1 micron, it is not possible to know whether any pigment particles are actually exposed or whether they are covered by a thin (approx. 1 micron) layer of plastic resin.

b) X-Ray Photon Spectroscopy of Surface of 3 mm dia. x 3 mm long Pellets

X-Ray Photon Spectroscopy (XPS) of resin pellets was carried out at the Surface Science Laboratory of the University of Western Ontario (Surface Science Western). XPS was used because it can examine the outermost surface of materials with penetration only of approx. 50A (Note: 1 micron equals 10,000A) and provide quantitative data.

The detailed results of the XPS work are in Appendix II.

In summary, the following conclusions were made (all concentrations are weight %):

i) In the PVC samples high concentrations of lead were detected at the external surface viz: 15% in Pb in the 33% lead chromate sample and 3.6% Pb in the 2% lead chromate samples. These levels were reduced by 90% after the measured surface was sputtered, i.e. cleaned to a depth of 100A by the x-ray flux. This indicates that higher levels of pigment are at the external pellet surface.

ii) In the PE samples the 50% $PbCrO_4$ pellets showed approx. 0.5 to 1.0% Pb at the surface. The 2% $PbCrO_4$ pellets showed approx. 0.2% Pb at the surface - at the detection limit of the method.

iii) In the 2% $PbCrO_4$ in ABS sample, lead pigment was not detected in any surface, at a detection limit of approx. 0.2% Pb (see c) ii) below).

There are several inconsistencies in the numerical values for atomic composition provided by XPS. For example, lead concentrations decrease after sputtering in the PVC samples but increase greatly in the PE sample. It is difficult to explain such effects based on the few samples examined.

c) **X-Ray Photon Spectroscopy of Surface of Lead Chromate Pigment Used in These Tests**

i) A non-encapsulated grade of pigment was used for the PE and PVC samples containing approx. 60% Pb. XPS of this pigment showed the surface composition to be:

17.2% by weight Pb
1.9% by weight Cr
13.8% by weight Al
36.2% by weight C
30.9% by weight 0

ii) A silica-encapsulated grade of lead chromate pigment was used in the ABS sample and was also examined by XPS. The surface composition found was:

27.6% by weight 0
35.1% by weight C
23.9% by weight Si
13.4% by weight Al
Lead was not detected.

Sputtering of the surface to remove the original surface and re-examination did not detect the presence of lead.

Therefore based on this limited test, this pigment is clearly coated with a silicate material which appears to encapsulate the lead chromate pigment entirely.

d) **Simulated Stomach-Acid Extraction of Lead Chromate-Containing Resins and Pigments**

Samples were extracted with 5% aqueous hydrochloric acid at 20°C for ten minutes according to the method described by Consumer and Corporate Affairs Canada in the Hazardous Products Act, Part 1, Section 9. Work was done by Technitrol Canada Ltd., Report No. 194363, 1989 August 25. Results were:

Sample	% Pb in Resin	ppm wt. of Pb* Leached	Proportion of Total Lead in Sample Extracted by Acid as %
33% $PbCrO_4$ in PVC	19.8	202	0.10
2% $PbCrO_4$ in PVC	1.2	8	0.07
50% $PbCrO_4$ in PE	30.0	249	0.08
2% $PbCrO_4$ in PE	1.2	4	0.03
3% $PbCrO_4$ in ABS	1.8	27	0.15
2% $PbCrO_4$ in ABS	1.2	7	0.06
			Average of above values = 0.08
Regular $PbCrO_4$ Pigment	60	9400	1.57
Encapsulated $PbCrO_4$ Pigment	40	6900	1.73

* ppm Pb is calculated on weight of sample pellets/pigment.

2. COMMERCIAL POLYETHYLENE RESIN CONTAINING 0.5 TO 1.0% AZODICARBONAMIDE

a) Dust Production by Attrition of Resin Pellets

Resin in the form of approx. 5 mm dia. lens-shaped pellets, produced by melt cutting, was tested to simulate attrition caused by pellets impacting other pellets or impacting metal surfaces such as in bulk containers and pneumatic conveying lines.

A one-gallon steel paint can was half-filled with resin and rolled at 60 rpm for one hour. The resin was then screened to measure dust production with results:

% weight Through 18 mesh and Retained on 80 mesh (177 micron opening)	% weight Through 80 mesh
0.0096	0.0012

b) Composition of Fine Dust Produced

The particles less than 80 mesh were examined by infrared microscopy. In this method infrared spectra are produced for individual particles. The spectra showed the material to be principally polyethylene with small levels of azodicarbonamide present. Thus the azodicarbonamide (which is a respiratory sensitizer) is bound in the polyethylene resin. Free particles of azodicarbonamide were not detected.

3. DUST IN REGRIND SAMPLES OF ABS, PVC AND HDPE RESIN

Samples of resin from a commercial regrind operation were collected directly from the grinder discharge and the size range measured at Queen's University. Results were:

		% weight retained on sieve				
Resin	Mesh Opening	5 Mesh (4 mm)	18 Mesh (1 mm)	100 Mesh (150 micron)	200 Mesh (75 micron)	Less than 200 Mesh
ABS		9.6	89.7	0.65	0.0013	Nil
PVC		48.5	51.2	0.3	Nil	Nil
HDPE		41.7	57.6	0.68	0.002	Nil

Airborne particles which can be inhaled must be less than 100 micron in size. This is known as "inspirable" dust (see ACGIH TLV Booklet, App. E). The fraction between 100 micron and 10 micron in size will be deposited in the upper respiratory tract and will usually be swallowed with the mucus. Particles less than 10 micron in size will be deposited in the mid-respiratory tract and lungs.

The data show that only 13 to 20 ppm by weight of regrind resin is less than 150 micron in size. No detectable quantities of dust less than 75 micron could be measured.

DISCUSSION

1. CORRELATION BETWEEN XPS/SEM AND ACID EXTRACTION TESTS

The acid extraction test simulates the extraction of ingredients from samples that could occur if the samples were ingested and subjected to stomach acid. The data in the Table above show clearly that the amount of lead extracted from resin pellets is proportional to the lead content and also particle size. The surface area to volume ratios for pellets and pigment particles are:

3 mm dia. x 3 mm long pellet
volume = 21.2 mm^3
surface area = 42.4 mm^2
Therefore surface area : volume ratio = 2.1 mm^{-1}

10 micron dia. pigment agglomerate
volume = 0.52×10^{-6} mm^3
surface area = 3.14×10^{-4} mm^2
Therefore surface area : volume ratio = 6×10^{2} mm^{-1}

Note: Selection of 10 micron size for the agglomerate is a simplifying assumption.

Therefore pigment particles have a surface area to volume ratio approx. 300 times greater than the pellets.

The greater surface area of pigment particles should enhance their solubility in acid, however, it is not possible to make a direct comparison with pellets due to unknowns such as solubility rate and presence of some aluminum-containing coating on the pigment particles, as indicated by the XPS analysis - see page 5.

About 0.08% of the total lead present in pellets was extracted compared to approx. 1.6% for the lead chromate pigment, i.e. a ratio of 20:1 for pigment : pellets.

Although the XPS measurements showed no detectable Pb at the surface of the encapsulated pigment and very low to non-detectable Pb levels at the surface of the PE and ABS samples, lead was still extracted from these materials in the hydrochloric acid test. Therefore there is no good correlation between XPS results and HCl extraction test results with respect to the availability of the lead pigment.

2. ARGUMENTS AROUND THE 0.1% INGREDIENT CUT OFF CONCENTRATION

$PbCrO_4$ present at <0.1% weight in a resin would not be subject to WHMIS regulations. 0.1% $PbCrO_4$ is equivalent to 0.06% Pb, assuming the material to be $PbCrO_4$. Is it possible to demonstrate that the lead in these materials which is in an available form, is less than 0.06% (600 ppm weight) Pb?

i) Composition of Dust from Resin

The SEM micrographs show that the lead pigment is at or very close to the pellet surface. The XPS measurements show that lead pigment content of the outermost pellet layer varied greatly with the resin used, being highest for PVC. This is probably a function of the dispersibility of the pigment in each resin, the melt viscosity characteristics, and the manufacturing process used. It is probable that different results would be achieved with the same nominal composition but different pellet manufacturing techniques.

Therefore we cannot extrapolate reliably from these data to estimate the pigment content of dust produced by pellet attrition.

Assume that dust has the same composition as the bulk resin.

ii) Quantity/Percentage of Inspirable Dust Produced from Resin or Regrind Material

Data obtained show:

- Attrition of PE pellets for one hour produced 12 ppm weight of dust less than 177 micron particle size, i. e. inspirable dust.
- Grinding ABS, PVC and HDPE scrap produced 13 to 20 ppm of dust less than 150 micron particle size.

Thus in all four samples the inspirable dust is well below 0.1% by weight. Therefore, regardless of the composition of this dust, it can be claimed that the "available" pigment which could cause worker exposure is well below 0.1% and therefore the material should be excluded from WHMIS classification.

The level of inspirable dust produced by a wide range of resins is not known. Therefore the broad applicability of this argument is not known.

iii) Percentage of Lead Extracted from Resin by 5% HCl

In all cases for resins tested by extracting whole pellets with 5% aqueous HCl at 20°C (see Table) the amount of Pb extracted was well below 0.06% Pb (= 0.1% $PbCrO_4$) calculated on a pellet basis.

Therefore the "available" pigment is below 0.1% and provided that this test is an acceptable criterion for extractability, the material should be excluded from WHMIS classification. The extraction level for smaller resin particles and for other formulations is not known, and therefore the broad applicability of the argument is not known.

3. HOW RELIABLY CAN A SUPPLIER PREDICT USES FOR PLASTIC RESIN PRODUCTS?

Arguments have been made that the use of professional judgement, in classifying resin products based on the potential for exposure, is not valid because suppliers cannot understand or predict end uses to which customers may subject their products.

This is an important and basic issue which SPI must deal with in a positive manner. Arguments that plastic resin suppliers can reasonably predict end uses include the following:

- Plastic resins have limited high temperatures for use consistent with preserving the useful, physical properties of the resin. At excessively high temperatures, plastics decompose or depolymerize producing a variety of low molecular byproducts and the hazardous consequences of such high temperature treatment are described on MSDS.

- Resins are sold in granular form, have particle sizes ranging from cylindrical pellets approx. 1/4" diameter, to spherical beads, to free flowing powder. Customers may grind resin to produce fine particles for unusual purposes and the adverse or hazardous consequences of grinding resin should be known to the supplier and described on MSDS.

- Commercial plastic resins are relatively chemically inert and MSDS should describe their chemical reactivity and incompatibility.

It is difficult to identify any other end use issues apart from temperature, size reduction and chemical reactivity which could apply to plastic resins.

If these three topics cover all significant end use issues then it should be possible to claim that suppliers can confidently consider end uses in using professional judgement to make WHMIS classifications.

4. DISCLOSURE OF GENERIC CHEMICAL IDENTITY OF HAZARDOUS INGREDIENTS IN PLASTIC RESINS

In cases where the detailed identity and concentration of hazardous ingredients in resins is not disclosed because WHMIS exemption if claimed, it is recommended that the generic chemical identity of these ingredients be provided so that users may take appropriate precautions in the event of fires, disposal by incineration, contamination of soil or water, etc.

APPENDIX I

SCANNING ELECTRON MICROSCOPY OF PLASTIC RESINS CONTAINING LEAD CHROMATE PIGMENT

A summary of conclusions obtained from SEM photomicrographs is given below. Photographs of the Polaroid photomicrographs are also provided (not included).

DEFINITION OF TERMS USED ON PHOTOMICROGRAPHS

SEI = Secondary Electron Image
= Surface Topography

BSE = Back Scattered Electron Image
= More dense particles at or near surface show up as lighter on background

Pb MAP = Light coloured spot identifies Pb-containing material - at or near surface

In SEM the electron beam penetrates the surface and causes backscattering. Penetration is a function of density of material and may be up to approx. 1 micron = 10,000 A.

2% $PbCrO_4$ in ABS

SEM by Queen's University

1. Cylindrical Surface

BSE image shows pigment particles at, or close to, surface and corresponding to high points on secondary electron image (SEI). Pb MAP confirms that particles contain Pb and correspond to SEI and BSE image.

2. Fractured Surface

BSE matches SEI for location of pigment particles. Number of particles is not significantly different from cylindrical surface at same magnification.

$PbCrO_4$ in PE

SEM by Queen's University

1. 50% $PbCrO_4$

a. Cylindrical Surface

Pigment particles visible at/near surface by SEI and BSE. Pb MAP inconclusive - not exposed long enough (see #1, 2).

b. Fracture Surface

Pigment particles visible at/near surface by SEI and BSE. "Pits" visible at fracture point where pigment particles were located. Pb MAP inconclusive since not adequately exposed (see #4, 5, 7).

c. Flat End of Pellet

Pigment particles visible at/near surface by SEI and BSE. Pb MAP inconclusive. Structures like pits visible (see #8, 9).

2. 2% $PbCrO_4$

a. Cylindrical Surface

Pigment particles visible at/near surface by SEI/BSE. Pb MAP confirms particle identification (see #11, 12, 13).

b. Flat End of Pellet

Pigment particles visible by SEI (see #14).

$PbCrO_4$ in Polyethylene (PE)

SEM by University of Western Ontario

1. 50% $PbCrO_4$

Cylindrical Surface

Pigment particles visible at or near surface. SEI only. No BSE or Pb MAP made (see photos #33, 34, 35).

2. 2% $PbCrO_4$

a. Cylindrical Surface

Pigment particles visible at/near surface by SEI. Pb MAP not very clear but supports identification. High mag. view shows particles bound in resin (see photos #22, 23, 25).

b. Fracture Surface

Pigment particles visible at/near surface by SEI. Pb MAP supports identification. Pigment particles more visible, i.e. at surface, than at cylindrical surface. "Pits" visible where pigment particles were located (see photos #26, 30).

$PbCrO_4$ in PVC

SEM by Queen's University

1. 2% $PbCrO_4$ - SEM Cylindrical Surface - Sample M

High pigment level at or close to surface. Pb MAP confirms BSE location of pigment particles (see #1001, 1003, 1002, 1004, 1005).

2. Fractured Surface

Appears to be less pigment than at surface.

33% $PbCrO_4$ - SEM - Sample N

Cylindrical Surface

Very high pigment level at or close to surface. Some surface occlusions in one view. BSE confirms high pigment at/close to surface.

APPENDIX II

X-RAY PHOTON SPECTROSCOPY OF PLASTIC RESINS CONTAINING LEAD CHROMATE PIGMENT

A summary of conclusions obtained from XPS analysis of resins is given in the attached Surface Science Western report dated August 1989.

Note:

XPS provides quantitative results in Atom % not weight %.

Atom % is converted to weight % by multiplying atom % by element atomic weight and normalizing these values to calculate % weight by each element involved.

XPS Analysis of Plastic Resin Pellets

For

Dupont Canada Inc.
Research Centre
Kingston, Ontario

By

Surface Science Western
University of Western Ontario
London, Ontario

August, 1989

Prepared by:
Dr. R. Foerch
R.D. Davidson

NOTE: A FEW REFERENCES TO WORK ON NON-SPI SAMPLES HAVE BEEN REMOVED FROM THIS REPORT.

Introduction

Pellets of PVC, PE and ABS containing various levels of lead chromate ($PbCrO_4$) have been analyzed by X-ray photoelectron spectroscopy (XPS or ESCA) to determine the levels of lead actually on the surface of the pellets. Techniques such as IR and SEM have indicated high levels of Pb present on the surface, however both these techniques probe beyond depths of several hundred Angstroms into the sample, thus probing the bulk polymer as well as the surface. XPS, on the other hand probes the first few monolayers to an approximate depth of 30-50 Angstroms.

During XPS analysis a sample is irradiated with monochromatized X-rays of known energy causing the ejection of photoelectrons from all elements (except hydrogen) within the sample. The kinetic energy (E_{KE}) of the ejected electron is equal to

$$E_{KE} = E_{Al\ K\alpha} - E_B - \Phi$$

Where $E_{Al\ K\alpha}$ = energy of the incident photon and
E_B = binding energy of the electron / eV
Φ = work function (usually negligible)

Thus, by measuring E_{KE} of the photoelectron and knowing $E_{AlK\alpha}$, E_B can be calculated. XPS provides both qualitative and quantitative information on the elemental composition of the sample.

Experimental

X-ray photoelectron spectroscopy was performed on the polymer pellets using an SSX-100 Surface Science Laboratory X-ray photoelectron spectrometer which utilizes monochromatic Al Kα X-rays for excitation of the samples. The elemental broad scans were recorded using a pass energy of 148.00eV and an X-ray spot size of 1000μm or 600μm analyzing binding energies between 0 and 1000eV.

Samples A1, A2, B1, B2 and C2 were analyzed on the cylindrical, the end and on a fractured surface. On A1, A2 and B2 the cylindrical surface was sputtered for 2 minutes using Argon to probe deeper into the surface. B1 was sputtered on the fractured surface.

Results

XPS results have been tabulated in Table 1 and values are given in atomic %. They appear to indicate that when the bulk polymer is PVC, lead is detected even at a

concentration by weight of 2%. On the other hand if the bulk polymer was PE, lead is detected at a concentration level by weight of 50%, but is not detected if the concentration level is 2%. However, when the bulk polymer is ABS, no lead is detected.

Samples A1, A2, B1 and B2 show levels of Pb on the cylindrical surface ranging from 1.2% to 0.01% which represents the detection limit of XPS for Pb. Upon sputtering the cylindrical surface (A1, A2, B2) for 2 minutes using Argon (to roughly a depth of 100 Angstroms), the amount of Pb very noticeably decreases suggesting lesser amounts of Pb further into the surface. Other elements detected were chlorine, silicon and very low levels of chromium in B1. Barium and cadmium were detected in sample A2.

Analyzing the end surfaces of samples A1 and A2, similar levels of Pb were observed as on the cylindrical surfaces. B1 shows slightly more Pb on the end surface of the pellet, while B2 shows no Pb.

Fractured surfaces of A1, A2 and B2 show similar levels of lead compared to the cylindrical surfaces. B1 shows a similar level of Pb on the fractured surface as on the outside cylindrical surface. When sputtering the fractured surface, XPS indicates an increased level of both Pb and Cr being exposed from further inside sample B1. Chromium was also be detected on A1 (cylindrical surface) and B1 (end and sputtered fracture).

Sample C2 was extremely "clean", showing no Pb or Cr on any surfaces examined, even after sputtering. However, it was noticed that upon sputtering the relative % of N and O on the surface decreased. Otherwise all surfaces showed similar amounts of O and N.

SEM Results

A series of secondary electron SEM micrographs were obtained from samples B1 and B2. The micrographs are identified on an attached sheet, Table 4.

The micrographs clearly show the difference in the pigment loading levels between 2% and 50% $PbCrO_4$ in the PE samples. The pigment particle size is approximately 0.5 - 1.0µm. The differ nt contrast levels for the particle (from bright white to a faint grey) suggest that the particles are at different depths within the matrix material. Pb X-ray

mapping was carried out on the 2% $PbCrO_4$ sample. The results show Pb, as expected, associated with the pigment particles.

Conclusion

The XPS results indicate that lead ($PbCrO_4$) is present in small amounts on the surface of $PbCrO_4$ doped PVC pellets. Upon sputtering deeper into the surface less Pb is detected. The concentration of Pb on the fractured surface is very similar to that on the cylindrical side, suggesting that the lead is present on the surface.

Pb is detected in very small amounts in the $PbCrO_4$ doped PE, even for the 50% doped pellets. The fractured surface shows similar amounts of Pb, yet upon sputtering, the concentration of Pb clearly increases. This indicates that even though some Pb is present on the surface, the majority is deeper inside the sample.

In the $PbCrO_4$ doped ABS, lead and chromium are not detected on any surface.

Recommendations

The objective of this preliminary study was to determine if $PbCrO_4$ pigment particles were exposed at the surface of the plastic resins. Intriguing XPS results, especially for the PVC samples, suggest that the pigment is concentrated at the surface. Further characterization with XPS and SEM may result in a better understanding of the location of the pigment particles in the PVC.

It may be possible to carry out further SEM examination using stereo imaging to determine whether or not the pigment particles are standing proud of the surface. Further XPS analysis on additional samples may aid in this study. For example, XPS analysis of freshly fractured (perhaps cooled to liquid N_2 temperatures) resin pellets would provide a good 'bulk' analysis to compare to the extruded cylindrical surfaces.

NOTE: THESE VALUES ARE IN ATOMIC %

Table 1. XPS analysis of $PbCrO_4$ containing polymer pellets.

sample	%C	%N	%O	%Cr	%Pb	%Cl	%Si	%Ba	%Cd	CALCULATED % WEIGHT Pb
A1 33% $PbCrO_4$ in PVC										
cylindrical side	82.7	-	10.1	0.2	1.2	5.0	1.0	-	-	15.4
cyl. side sputtered	91.5	-	8.1	-	0.1	0.4	-	-	-	1.7
endview	86.3	-	12.4	-	1.3	-	-	-	-	18.0
fractured	79.2	-	9.7	-	1.1	10.0	-	-	-	13.5
A2 2% $PbCrO_4$ in PVC										
cylindrical side	78.6	-	9.3	-	0.3	10.4	-	0.8	0.7	3.6
cyl. side sputtered	91.2	-	3.4	-	0.04	5.3	-	0.1	-	0.6
endview	84.3	-	9.1	-	0.2	5.4	-	0.5	0.5	2.7
fractured	72.2	-	4.7	-	0.1	22.9	-	0.2	0.1	1.2
B1 50% $PbCrO_4$ in PE										
cylindrical side	97.3	-	2.7	-	0.03	-	-	-	-	0.5
endview	96.1	1.2	2.2	0.05	0.1	-	0.35	-	-	1.7
fractured	98.7	-	1.3	-	0.05	-	-	-	-	0.9
frac. side sputtered	93.3	0.3	4.5	0.8	0.6	-	0.6	-	-	4.0
B2 2% $PbCrO_4$ in PE										
cylindrical side	99.2	-	0.85	-	0.01	-	-	-	-	0.2
cyl. side sputtered	98.2	1.1	0.75	-	-	-	-	-	-	<0.2
endview	99.2	-	0.8	-	-	-	-	-	-	<0.2
fractured	100	-	-	-	-	-	-	-	-	<0.2
C2 2% $PbCrO_4$ in ABS										
cylindrical side	90.3	4.9	4.3	-	-	-	0.5	-	-	<0.2
cyl. side sputtered	95.1	2.0	2.9	-	-	-	-	-	-	<0.2
endview	92.1	4.6	3.3	-	-	-	-	-	-	<0.2
fractured	89.1	5.0	4.2	-	-	-	1.8	-	-	<0.2

NOT DETECTED

NOT DETECTED

CTL019178

THE FOLLOWING THREE SPECTRA ARE

TYPICAL OF THOSE OBTAINED

FOR $PbCrO_4$ - CONTAINING RESINS

X-Ray Power:

Flood Gun: 1.0

Operator: RF

Spot Size: 600 u

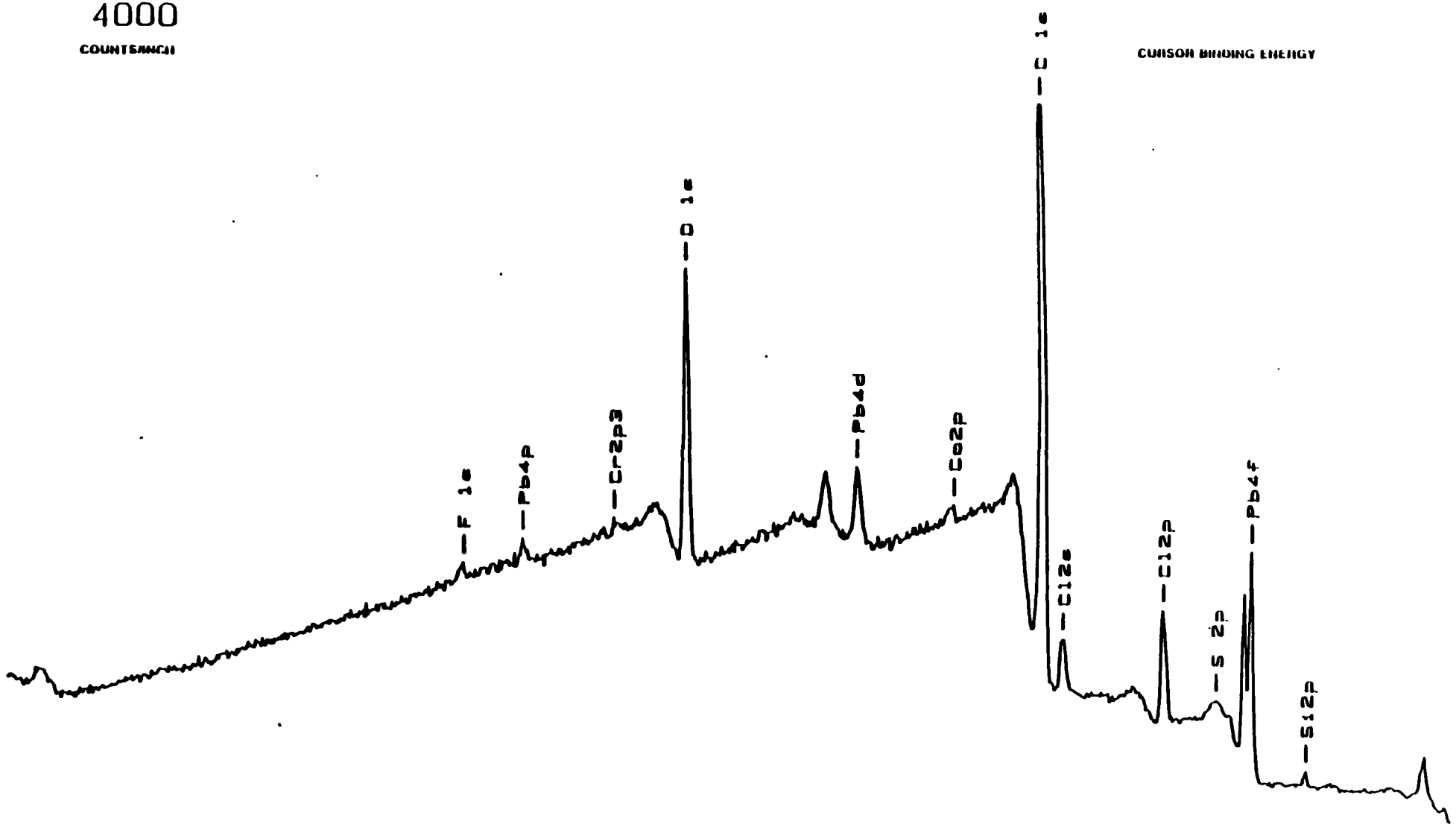
Resolution: 4

VERTICAL SCALE

4000

COUNTS/INCH

CURSOR BINDING ENERGY



electrons detected →

← binding energy (eV)

1000.0

UPPER BINDING ENERGY (eV)

0.0

LOWER BINDING ENERGY (eV)

SAMPLE: ..... Disc: B9836 ..... DATE: 8/15/1989

COMMENTS: ..... DATA FILE # ..... DUPON(A1) Region 1

LEAD CROMATE 33%/ PVC

2

SCANS

The Surface Science Laboratory, The University of Western Ontario

Report #:

CTL019180

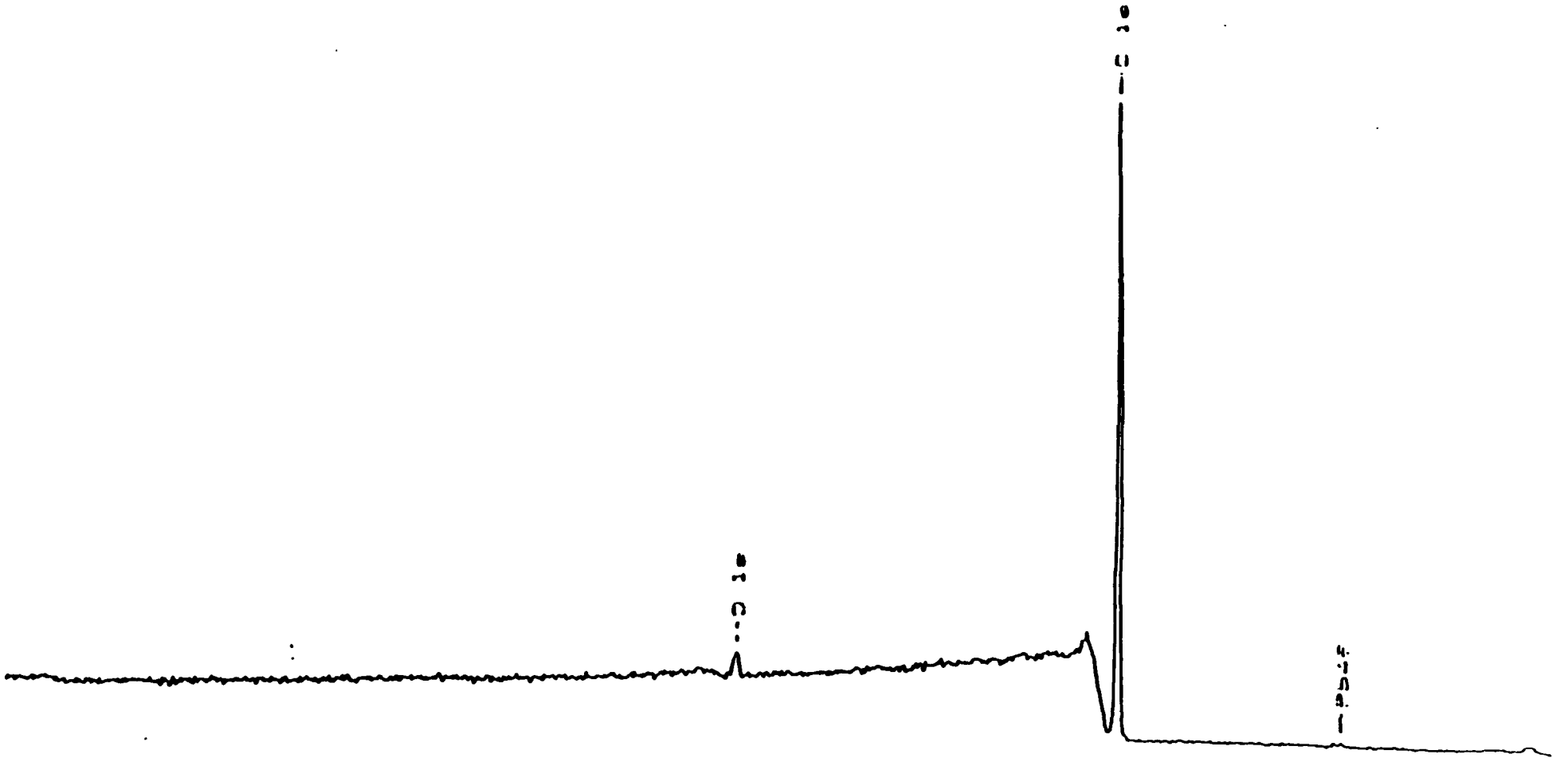
X-Ray P wer: Flood Gun: 1.0 Operator: RF Spot Size: 600 u Resolution: 4

VERTICAL SCALE

4000

COUNTS/INCH

CURSOR BINDING ENERGY



electrons detected →

1000.0

UPPER BINDING ENERGY (eV)

SAMPLE: Disc: 86636 DATE: 8/15/1988

COMMENTS: DATA FILE # DUPONT(B1)

LEAD CHROMATE 582 PE Region 1

← binding energy (eV)

0.0

LOWER BINDING ENERGY (eV)

3

SCANS

The Surface Science Laboratory, The University of Western Ontario

Report # CTL019181