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HEALTH STANDARDS FOR LEAD CHROMATE DUST

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Abstract—Combined environmental and medical investigations in pigment industries in the Netherlands suggest that the same hygienic standard applies to all lead pigments, if air pollution is caused by dusts. Paint technology offers a possible explanation for a lower toxicity of lead chromate in paints.

INTRODUCTION

AMONGST industrial hygienists there is a strong tendency to regard lead chromate as considerably less toxic than many other lead compounds. The investigations reported by HARROLD, MEEK, COLLINS and MACKELL (1944) and by HARROLD and MEEK (1949) particularly emphasized the lower toxicity of this compound. According to these authors the M.A.C. for Pb might possibly be multiplied by a factor 10, if this element was present as lead chromate. They based their opinion on the results of a carefully conducted combined medical and environmental investigation of 185 workers, who sprayed lead chromate paints: notwithstanding high Pb concentrations in the air, no significant increase of Pb excretion and of basophilic aggregation took place. This fact was in sharp contrast with their experiences in departments polluted with other lead compounds. HARROLD (1949) determined the solubility of lead chromate and carbonate in water, pleura fluid and serum: the former compound was much less soluble. According to the authors this difference in solubility constitutes one of the main causes of the lower toxicity of lead chromate. ELKINS (1959) and HACKVALE (1959) suggested a M.A.C. of 0·5 mg Pb/m^3, if lead chromate is the polluting agent. Recently BROWNING (1961) also stated that lead chromate was undoubtedly less toxic than the more soluble compounds.

Other authors, however, expressed a more reserved opinion. FAIRHALL, MINOT and REZNIKOFF (1926) already suggested the possibility of transformation into more soluble compounds in the gastric and pancreatic fluid. According to CANTAROW and TRUMPER (1944) there is undoubtedly a possibility of absorption in the whole respiratory tract, also of less soluble lead compounds. LANE (1936) and HUMPERDINCK (1939) mentioned the formation of lead carbonate by CO_2 in the lungs.

BUCHANAN (1957) indicated another aspect: technical lead chromate often is not pure; orange lead chromate must be supposed to be more toxic than the yellow pigments, because in the added chrome red more than 25 per cent soluble lead sulphate is coprecipitated. According to DUTCH STANDARDS (N 901) chrome yellow is a mixture of lead chromate and lead sulphate. The dark yellow pigments are likely to contain at least 95 per cent, the medium pigments 70–95 per cent, and the bright pigments 45–70 per cent lead chromate; in any case the sum of lead chromate, lead sulphate and lead oxide must be 95 per cent or more of the material. Chrome

red is a basic lead chromate, chiefly $PbCrO_4 . Pb(OH)_2$; chrome orange is a mixture of chrome red and chrome yellow. All these compounds might be considered as *technical* lead chromate, although the composition may be somewhat variable.

In a combined environmental and medical investigation in the years 1957 to 1959, in three pigment factories (A: 81 workers, B: 80 workers, C: 21 workers) in the Netherlands, the authors investigated the relation between exposure to lead and the reaction of the human organism. In these factories there was exposure to several lead containing pigments: carbonate, sulphate, stearate, titanate, chromate. At the SYMPOSIUM on Maximum Allowable Concentrations in Industry in Prague (1959) the authors made a communication on the results of the investigation in factories A and B: if one wants to prevent a decrease in haemoglobin, the M.A.C. should be about 0·1 mg Pb/m³ of air, at least under the conditions in the pigment industries. The medical findings of factories A and B have extensively been published elsewhere (ZIELHUIS, 1959, 1961*a*, 1961*b*). It proved to be possible in factories B and C to examine a number (26) of persons working in departments in which exclusively chrome yellow was produced and processed. By relating the exposure of these 26 workers with the medical findings, an opinion could be formed as to the toxicity of lead chromate.

Method of investigation

The determination of concentrations of Pb and Cr in the inhaled air was done by the Industrial Air Pollution Division of the Research Institute for Public Health Engineering T.N.O. by sampling a volume of 1–3 m³ of air during ½–1 hr at a height of about 1·5 m above the floor near the workers' heads. The dust was collected on a paper filter (Schleicher and Schüll, no. 589^{III}, ϕ 9 cm). The filter was digested with a mixture of concentrated sulphuric acid, concentrated nitric acid and 30 per cent H_2O_2 solution. The lead was extracted from the obtained solution by a solution of dithizone in carbon tetrachloride and determined spectrophotometrically using a reversion method by measuring the absorption of the dithizone solution at a wave length of 620 mμ. The chrome content of the filters was determined by oxidizing the solution obtained after digestion of the filter with a $KMnO_4$ solution, adding diphenylcarbazide and measuring the absorption at 540 mμ. Both metals could be determined with an accuracy of about 1 μg.

The total number of samples that has been analysed for both Pb and Cr was 33 in factory A, 39 in factory B and 26 in factory C. During the sampling the filter was held in a vertical position. From the air velocity before the filter (about 18 cm/sec) and the dimension of the filterholder we can calculate that particles up to about 70 μ diameter will be sampled. The size-grading of the collected material could not be determined. In several other samples of dust, collected from the floor, from machinery, from rafters, etc., a size-grading has been done with an Andreasen–Esenwein pipette apparatus. These samples, which contain surely more coarse particles than the airborne dust, all contained 4–17 per cent (by weight) particles smaller than 5 μ. Some additional information has been gained by dust determinations done in the same place and at the same time with thermal precipitators. The average number of particles $< 5\ \mu$ in diameter per cm³ of air was between 300–800 as counted under the microscope with a magnification of 560× in darkfield. These results will not be discussed further.

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The occupational history of the workers was assessed by interview; data were collected as completely as possible on recent working place and on past exposures to lead.

The department for occupational medicine of the Netherlands Institute for Preventive Medicine made an investigation into the health of the workers in the same periods as the determination of exposure was made. The medical investigation included:

—medical history
—physical examinations
—laboratory investigations:
haemoglobin (according to Sicca)
number of basophil punctate erythrocytes in dark ground illumination (ZIELHUIS, 1957)
coproporphyrinuria semiquantitatively (DONATH, 1956) with a scale as follows: 1: 0–50 μg/l.; 2: 50–100 μg/l.; 3: 100–200 μg/l.; 4: 200–400 μg/l.; 5: 400–800 μg·l.; 6: 800–1600 μg/l.; 7: >1600 μg/l.

In the three factories a total of 182 male workers, who were not clinically ill, was examined. In this communication only some of the data of 26 workers (B: 23 workers; C: 3 workers), almost exclusively exposed to chrome yellow, are reported.

By means of the investigations mentioned above, which were conducted in each factory in the same period of time, the degree of exposure and the reaction of the organism were *independently* assessed by different teams.

RESULTS

In graphs 1, 2 and 3 the corresponding Pb and Cr concentrations in individual samples have been plotted for factories A, B and C. In factory A there is no clear correlation between Pb and Cr concentrations. In factories B and C there is a very good correlation: the ratio Pb/Cr is 6·2 in factory B and 5·5 in factory C.

For all workers, working in those departments of factory B or C, in which the exposure to lead chiefly was caused by the presence of chrome yellow, the average exposure to lead was calculated from all Pb concentrations that have been measured. The workers could be divided into three classes of exposure:

class *a*: 7 workers, exposure generally less than 0·1 mg Pb/m^3;
class *b*: 5 workers, exposure generally between 0·1 and 0·2 mg Pb/m^3;
class *c*: 14 workers, exposure generally more than 0·2 mg Pb/m^3

In graph 4 the data for haemoglobin (in g per cent), basophilia (per thousand) and for coproporphyrinuria (degrees acc. to DONATH) have been plotted in absolute numbers for classes *a*, *b* and *c*, and in procentual values for workers (n = 117), who had never been exposed to lead in their occupation.

There is a consistent trend of deterioration of the laboratory values (decrease of haemoglobin and increase of coproporphyrinuria and basophilia) with increasing exposure to lead chromate dust.

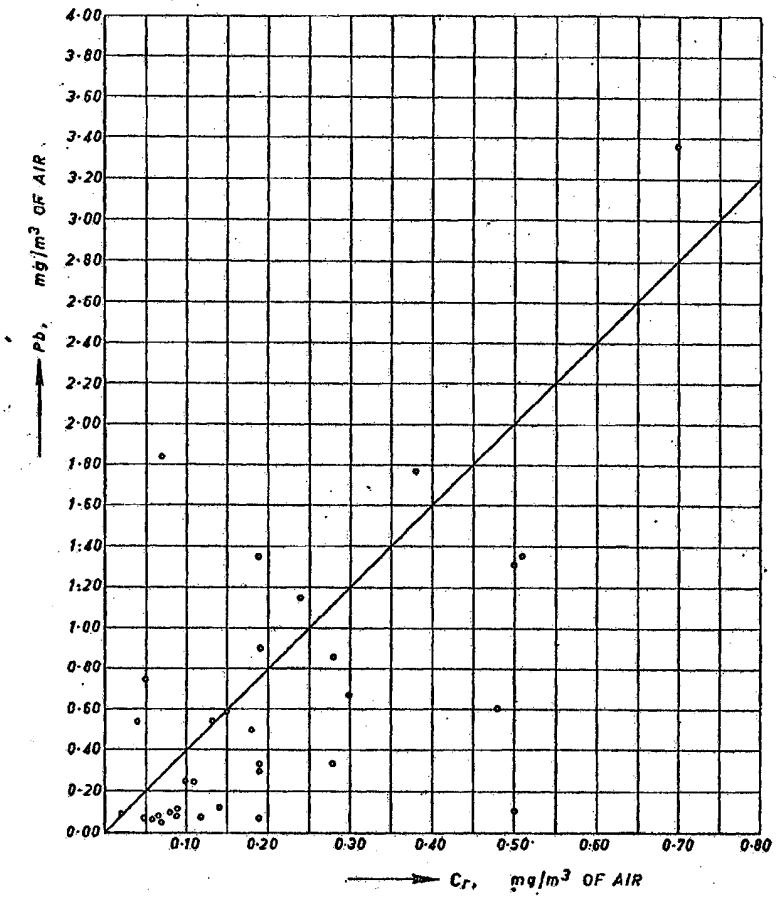
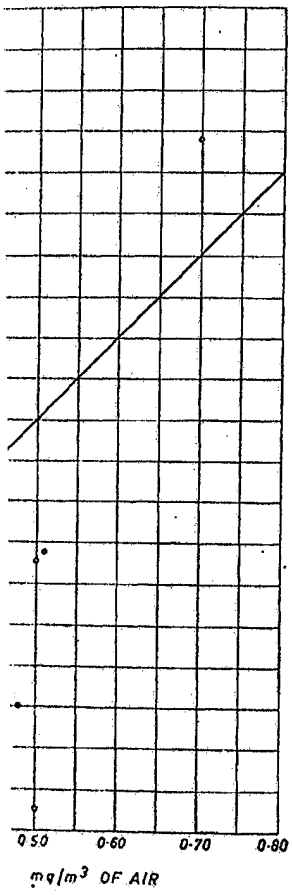


FIG. 1. Factory A.



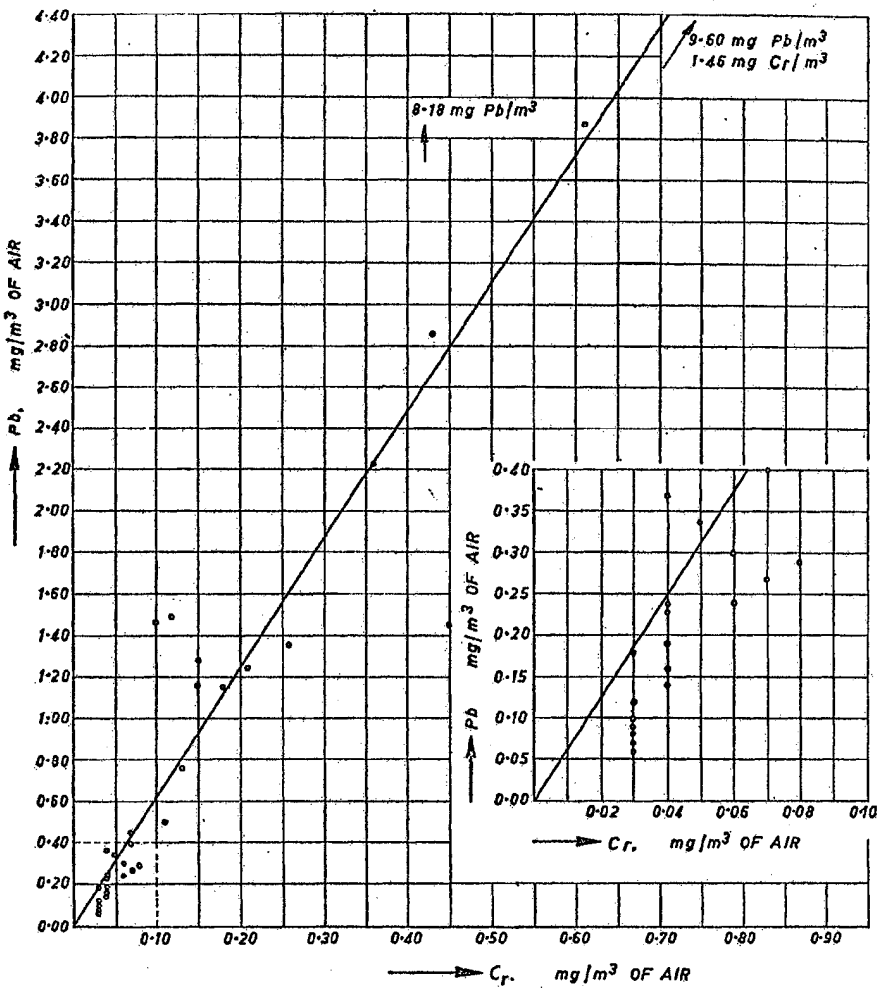


FIG. 2. Factory B.

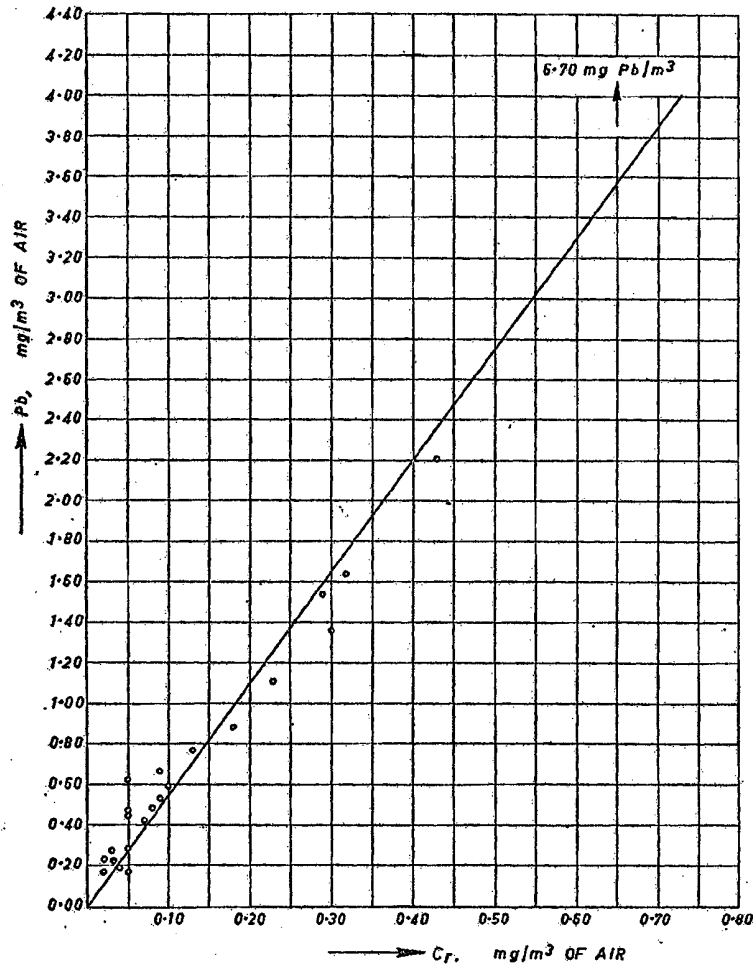
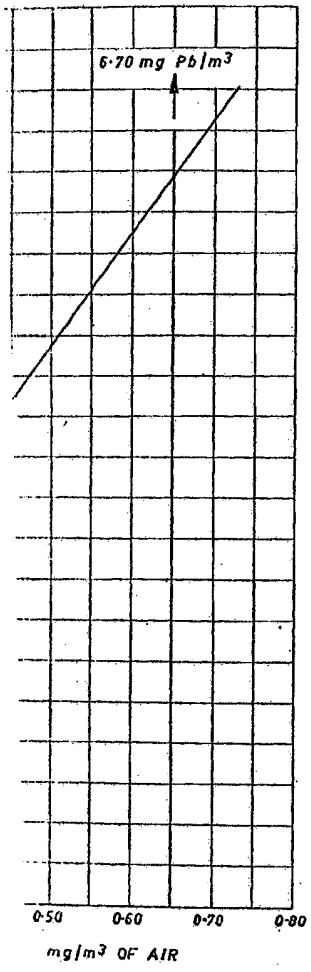


FIG. 3. Factory C



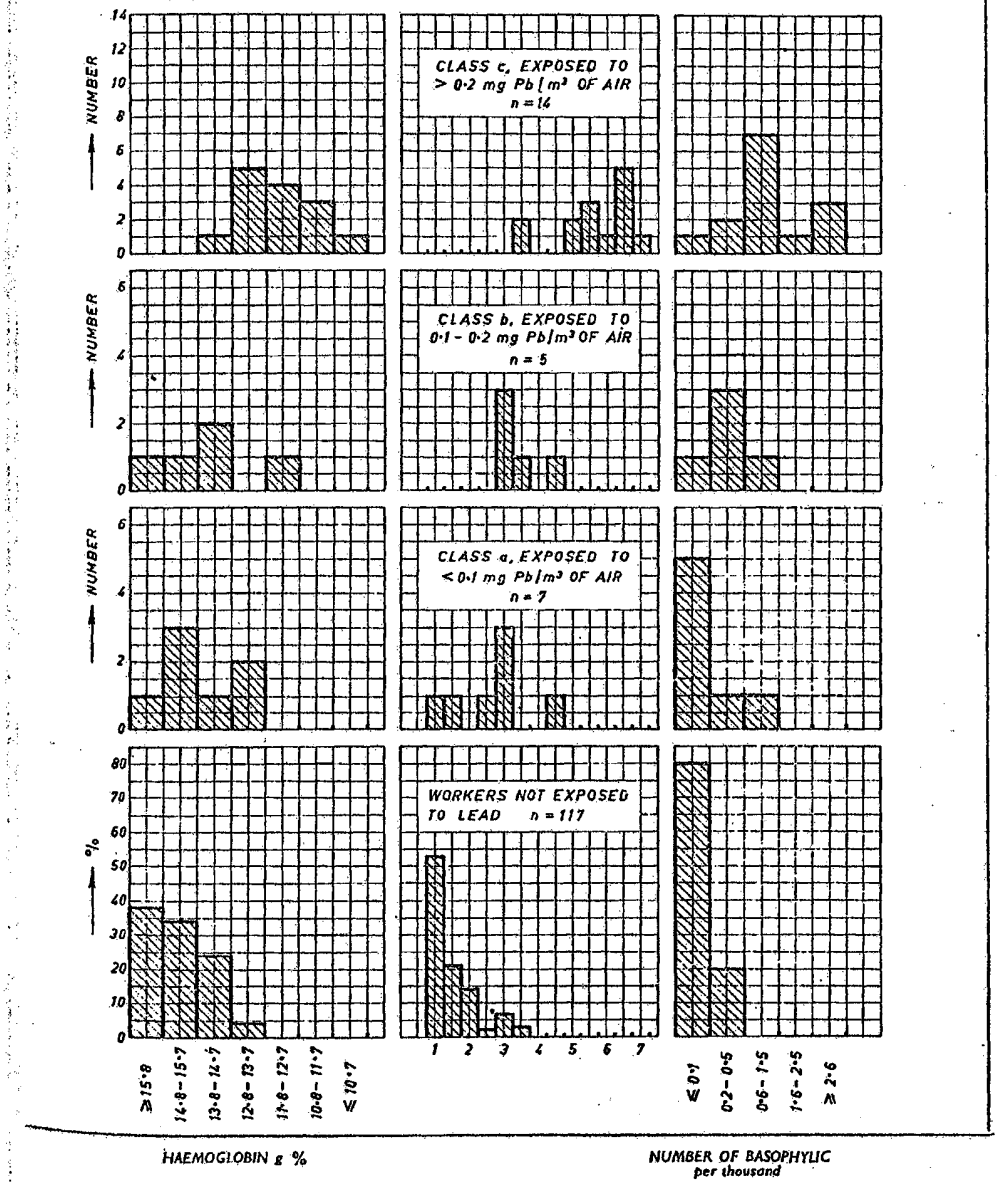


Fig. 4. Laboratory data in relation to lead concentrations in air, in workers exposed to Chrome Yellow.

DISCUSSION

The ratio Pb : Cr has only been determined in those premises, where chiefly lead chromate in the air could be expected. In pure $PbCrO_4$ this ratio is 4·0. In most chrome yellows a part of the lead will be present as $PbSO_4$ and, to a very slight extent as PbO. Therefore this ratio may well be more than 4·0. A ratio of less than 4·0, however, shows that other chrome compounds were present.

In graph 1 the concentration of Pb and Cr found in different departments of factory A, are plotted together. The ratio Pb : Cr differs over quite a large range. The lead therefore has not been present chiefly as chrome yellow. There was also a production of white lead, of lead stearate and of zinc chromate. Therefore the data obtained in this factory are not discussed further in the paper.

In graph 2 the data obtained in factory B are plotted. Here we observe a strong tendency for these concentrations to scatter around a straight line, which corresponds with a ratio Pb : Cr of 6·2. A chrome yellow with a ratio Pb : Cr = 6·2 will approximately consist for two thirds of $PbCrO_4$ and for one third of $PbSO_4$. We concluded from these data that in these departments of this factory about two thirds of the lead intake of the workers (n = 23) will consist of lead chromate.

In graph 3, finally, the Pb and Cr concentrations found in three departments of factory C are plotted. Here the ratio Pb : Cr is to a high degree constant at 5·5, corresponding with a chrome yellow, threequarters of which consists of $PbCrO_4$ and one quarter of $PbSO_4$. This ratio corresponds very well with the ratio Pb : Cr in a sample of the chrome yellow that was made and worked up in this factory at the time of the investigation. We concluded from these data that in these departments three-quarters of the lead intake of the workers (n = 3) will be lead chromate.

We did not give the data from medical history, physical examination and duration of exposure (occupational history), because for the total investigated population no significant correlation existed between symptoms or signs (exclusive lead line) and the degree of exposure; nor could a correlation be established between the medical data and duration of exposure (exclusive the first months) (ZIELHUIS, 1959). In sharp contrast to this the laboratory data (Hb, basophilia, coproporphyninuria) correlated significantly with the degree of air pollution, determined in the same period of time. It may be stated that the general conditions in these factories had not changed remarkably over the last few years.

Graph 4 suggests an evident correlation between the reaction of the haemopoetic system and the degree of air pollution to chrome yellow. In class *a* the coproporphyrinuria already differs significantly from the norm. The slight downward trend in Hb in this class may be related to lower socio-economic status (the basophilia and coproporphyrinuria do not respond to this; ZIELHUIS 1959). Both the coproporphyrinuria and basophilia in class *b* clearly deviate from the norm, whereas in class *c* this trend is still more pronounced. The haemoglobin in class *c* is also clearly sub-normal. If we take the decrease of haemoglobin as the criterion for establishing the M.A.C. value for lead compounds, we may conclude to a M.A.C. of 0·1–0·2 mg Pb/m³ if the exposure is mainly to lead chromate. Owing to the small number of persons, whose present and past exposure chiefly was to lead chromate dust, it is not quite possible to state according to this criterion whether the M.A.C. for lead chromate should be 0·1 or 0·2 mg Pb/m³. In any case this *M.A.C. is of the same order of magnitude as the M.A.C. for other lead compounds.*

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HARROLD *et al.* suggested pure lead chromate to be 10 times less toxic than lead carbonate; ELKINS mentioned a factor 3. The results of the total investigated population suggested a M.A.C. of 0·1–0·2 mg Pb/m³ (0·15 mg Pb/m³) for all lead pigments. According to HARROLD the M.A.C. for technical lead chromate as produced in factories B and C (threequarters to two thirds pure, i.e. about 70 per cent) might be expected to be: $10\times0{\cdot}7\times0{\cdot}15+0{\cdot}3\times0{\cdot}15 = 1{\cdot}1$ mg Pb/m³. Using ELKINS' factor a M.A.C. of $3\times0{\cdot}7\times0{\cdot}15+0{\cdot}3\times0{\cdot}15 = 0{\cdot}36$ mg Pb/m³ would result. These values are considerably higher than the value of 0·1–0·2 mg Pb/m³ as suggested by the present investigation. Workers exposed to over 0·2 mg Pb/m³ (as technical lead chromate) clearly showed evidence of clinical lead intoxication, e.g. decrease in haemoglobin.

It might be suggested that the above mentioned signs of lead intoxication were not due to lead chromate, but mainly due to more toxic, "soluble" impurities (e.g. lead sulphate). In that case using HARROLD's factor, a value of one tenth $\times 0{\cdot}7\times0{\cdot}15 +0{\cdot}3\times0{\cdot}15 = 0{\cdot}055$ mg "soluble" lead compounds per m³ might be expected as threshold limit to be in accordance with our results, and a value of 0·08 mg calculated with ELKINS' factor. These figures are considerably lower than the generally accepted values of 0·1–0·2 mg Pb/m³ for "soluble" lead compounds. The fact that the same M.A.C. has been established in departments mainly polluted with technical lead chromate and in departments polluted with other lead pigments, strongly suggests a *similar toxicity of all lead pigment dusts*, soluble and "unsoluble". The factors of HARROLD *et al.* and of ELKINS do not seem to be valid in the investigated situation, i.e. in the case of exposure to chrome yellow dust.

HARROLD *et al.* investigated workers who *sprayed* lead chromate containing paints. In these paints the pigment particles are coated by a layer of vehicle. Owing to the acid reaction of lead chromate no chemical binding is formed between lead chromate and the vehicle; there is no formation of lead soaps. It will therefore be difficult for the organism to attack and to absorb the small paint droplets. According to this theory the acid lead sulphate present as an admixture in chromate paints, should also be little aggressive. There is an important difference from many other lead containing paints. Lead carbonate and minium are alkaline substances which form lead soaps such as lead linoleate, lead ricinoleate, etc. It is a well-known fact that organic lead compounds from fatty acids are well absorbed. The different behaviour of lead chromate in paints presumably explains, at least partly, the lower toxicity of these paints, in contrast to many other lead containing ones. In the investigation in the pigment industries, however, an exposure to respirable lead chromate dust existed. The organism is directly exposed to this pigment itself and no vehicle interferes. In this case one has to consider the toxicity of lead chromate as similar to the toxicity of more soluble lead compounds.

REFERENCES

AUB, J., FAIRHALL, L. T., MINOT, A. S. and REZNIKOFF, P., (1926) *Lead Poisoning*. Williams and Wilkins, Baltimore.

BROWNING, E. (1961) *Toxicology of Industrial Metals*. Butterworth, London.

BUCHANAN, W. D. (1957) Toxic Hazards in the Paint Industry. *J. Oil and Colour Chem. Ass.* 40, 337.

CANTAROW, A. and TRUMPER, M. (1944) *Lead Poisoning*. Williams and Wilkins, Baltimore.

DONATH, W. F. (1956) Simple portable apparatus for the semi-quantitative determination of the coproporphyrinuria content in urine. *Arhiv. Hig. Rada*, **7**, 77.
ELKINS, H. B. (1959) *The Chemistry of Industrial Toxicology*; 2nd ed. Wiley, New York; Chapman and Hall, London.
HACKVALE, W. S. (1959) The control of a lead hazard in industry. *Occup. Health Rev.* **11**, 17.
HARROLD, G. C. (1949) Solubility of lead compounds in human pleural fluid and blood serum. *J. Industr. Hyg. and Tox.* **31**, 327.
HARROLD, G. C. and MEEK, S. F. (1949) Solubility and the relative toxicity of lead chromate *Ind. Med. and Surgery* **18**, 407.
HARROLD, G. C., MEEK, S. F., COLLINS, G. R. and MACKELL, T. F. (1944) Toxicity of lead chromate. *J. ind. Hyg. and Tox.* **24**, 47.
HOOFD CIE. NORMALISATIE IN NEDERLAND (1951) *Droge verfstoffen (pigmenten); definities en keuringsvoorschriften.* Normblad N 901.
HUMPERDINCK, K. (1939) Verwendung bleihaltiges Spritzlacken in der Leder und Kunstlederindustrie. *Arbeitsschutz* **8**, 270.
LANE, R. E. (1936) The prevention of industrial plumbism. *Lancet* **2**, 206.
SYMPOSIUM ON MAC IN INDUSTRY. Prague 1959, in press.
ZIELHUIS, R. L. (1957) Methods of counting basophil punctated erythrocytes in lead intoxication *Int. Congress on Occup. Health, Helsinki* **3**, 290.
ZIELHUIS, R. L. (1959) De industriële loodintoxicatie in Nederland; beschouwingen en onderzoekingen. *Proefschrift, Leiden.* Verhandeling Ned. instituut voor preaventieve geneeskunde, no. 46.
ZIELHUIS, R. L. (1961) Coproporyphyrinuria in groups of workers as an index of inorganic lead absorption. *Brit. J. industr. Med.* **18**, 58.
ZIELHUIS, R. L. (1961) Maximal zulässige Grenzwerte biologischer Reaktionen in der Verhütung gewerblicher Bleivergiftung. *Zentr. Arb. med. u. Arb. schutz.* **11**, 129.