

to minimize air pollution from chem. or power plants.

62469x Rapid continuous determination of nitric oxide concentration in exhaust gases. T. Singh, R. F. Sawyer, E. S. ... and L. S. Caretto (Univ. of California, Berkeley). *Environ. Contr. Ass.* 18(2), 102-5(1968)(Eng). The rapid determination of NO levels in exhaust gases is required both for lab. studies of exhaust emission characteristics of combustion engines and for routine inspection of motor vehicle exhaust. A continuous, rapid, continuous anal. method for measuring NO was demonstrated. Rapid oxidn. of NO to NO₂ is obtained through catalytic oxidation. NO₂ concns. are detd. by means of an uv absorption technique. NO concns. between 100 and 5000 ppm. were measured and response time of about 20 sec. obtained. The presence of unburned hydrocarbons in the exhaust sample has no effect on the results of this technique which requires only the removal of hydrocarbons or adjustment of O₂ concn.

RCXV

62470r The control of fumes from a hot blast cupola by high-pressure scrubbing without appreciable thermal buoyancy loss. Sullivan and R. P. Murphy. *Int. Clean Air. Congr., London 1966* (Pt. 1), 144-6(Eng). The control of fumes from some of the more recently developed metallurgical processes presents difficult problems. Choice of equipment is limited virtually to electrostatic pptn., fabric filtration, or high-energy scrubbing. The last is the least costly. From the air pollution point of view, steam production and loss of thermal buoyancy of the dust-laden gases are important disadvantages. A recent installation was designed in which the heat is extd. from the flue gas before scrubbing and re-introduced afterwards. As a result, a cooler and drier plume which has no tendency to down-wash was achieved.

George A. Robinson Sr.

62471s The biological effect of caprolactam and its sanitary toxic assessment as an air pollutant. I. M. Krichevskaya, V. I. Petrovsk. Med. Inst., Kemerovo. *Gig. Sanit.* 33(1), 22-8(1968)(Russ). The thresholds for detection of caprolactam in air, by odor, by electroencephalography, and by its effect on sensitivity of the eye are 0.3, 0.2, and 0.18 mg./m.³, resp. Exposure to 0.66 mg./m.³ for 82 days showed changes in motor chronaxy, cholinesterase activity, and coproporphyrin excretion. A concn. of 0.024 mg./m.³ did not produce any observed physiol. changes. The recommended max. permissible concn. both for a single and continued exposure is 0.06 mg./m.³.

John Howe Scott

62472t Asthma and isocyanates. J. M. Mantz, B. Hamada, J. D. Tempe, and A. Meyer (Serv. Reanimation Clin. A.C.H.U. Hop., Strasbourg, France). *Arch. Mal. Prof., Secur. Soc.* 28(9), 673-6(1967)(Fr). Some 65 cases of a peculiar type of asthma were noted in a Spanish plant dealing with Desmodur T, an isocyanate mixt. used in manuf. of synthetic rubbers, plastics, paints, etc. The effective constituents are toluene 2,6-diisocyanate, and the 2,4-isomer. This is a chem., since it has many free isocyanate groups, and is volatile at room temp. and, therefore, inhaled easily. Tests show that the particular symptoms are due to Desmodur T. Both irritation and allergy are discussed as causes, and the aromatic is thought to be more responsible than the isocyanate group. Desmodur II (hexamethylene diisocyanate) causes no symptoms. Since there is no treatment, only preventive measures are advised, including immediate removal of affected workers from the area where these isocyanates are handled; compulsory goggles, protective gloves and filters; control of the amount of chemical present. In previous work by Henschler, 0.02 mg./1000 is considered satisfactory. The authors consider 0.005 parts/1000 is better.

M. I. Rawnsley

62473u Hygienic features of the production process for alloys of less-common metals. I. V. Shalganova (I. Mosk. Inst. im. Sechenova, Moscow). *Gig. Sanit.* 32(12), 28-31(1967)(Russ). The following LD₅₀ in mg./kg. are reported for: K niobate, Ta₂O₅, and Nb₂O₅ all greater than 4000; ZrCl₄, 830.0; NaF, 97.0; K₂ZrF₆, 97.5; K₂TaF₇, 110.0; Fe₂O₃, 130.0. Exposure of guinea pigs for 4 months to atm. concn. of 10 mg./m.³ K₂ZrF₆ or K₂TaF₇ produced redns. in alkal. phosphatase, and albumin concns. in the blood.

John Howe Scott

62474v The toxicity of aerosols of sodium carbonate and sodium bicarbonate. A. L. Reshetnyuk and L. S. Shevchenko (Donetsk. Nauch.-Issled. Inst., Donetsk. Gig. Tr. Profzabol). *Gig. Sanit.* 33(1), 111-13(1968)(Russ). Rats exposed to an atm. concn. of 42 ± 3 mg./m.³ of dust obtained by spraying a Na₂CO₃ contg. sulfonol showed greater local morphologic changes in lungs and redns. in tissue ascorbic acid concns. than did rats exposed to atm. contg. 70 ± 20 mg./m.³ without the sulfonol. The recommended max. for atm. dusts contg. Na₂CO₃ is 5 mg./m.³ depending on whether an anionic surface active is present or not.

John Howe Scott

62475w The hygienic significance of small concentrations of ammonia in the atmosphere. N. R. Kosiborod (Novosibirsk. Nauch.-Issled. Sanit. Inst., Novosibirsk). *Gig. Sanit.* 33(1), 119-121(1968)(Russ). The thresholds for detection of Et₃NH in

the atm. by odor, by its effect on the sensitivity of the eye, and by electroencephalography are 0.084, 0.086, and 0.093 mg./m.³, resp. Rats exposed for 93 days to 0.4 mg./cu. m. showed slight changes in motor chronaxy, HS-concns., and cholinesterase activity which were accentuated by starving. An atm. contg. 0.04 mg./m.³ did not produce any observed effects. The recommended max. permissible concn. is 0.05 mg./m.³.

John Howe Scott

62476x A toxicological study of Bulgarian reactive dyes. I. V. Khristeva (Katedra higiena, Plovdiv, Bulg.). *Khig. Zdravopazhvanie* 10(4), 389-94(1967)(Bulg). The toxicity of new Bulgarian dyes used in the textile industry Hisalone orange (I) and Hisalone brilliant red (II) was tested in white mice and rats. Aq. solns. of I and II at concns. 5, 10, and 20% were administered intraperitoneally or orally. The LD₅₀ of I was found to be 435 in mice and 700 in rats; that of II was in rats 840 mg./kg. intraperitoneally. The LD₅₀ of I and II after oral administration were 14 and 15 g./kg., resp. Manifested dystrophic changes were observed after higher doses of I or II.

Petr Skrabanek

62477y Urinary excretion of nickel in subjects exposed during electrolytical production of nickel. I. Klucik and R. Kemka (Vyskumny Ustav Hyg. Prace, Bratislava, Czech.). *Bratislav. Lek. Listy* 48(9), 523-9(1967)(Slo). The urinary excretion in 6 persons decreased exponentially with time to 0.106 ± 0.048 on the 6th day and to 0.066 ± 0.020 γ Ni/ml. on the 7th day after terminated exposure to an atm. contg. 0.7-1.26 γ Ni/l. in the form of NiCO₃ and NiSO₄ aerosols. With regard to the av. Ni content in the urine of normal unexposed persons (0.098 ± 0.042 γ/ml.), the excretion process thus seems to require 6-7 days.

L. J. Urbanek

62478z The hygienic characteristics of trace element fertilizers (PMU-7) production dust. T. D. Lienko (I. Mosk. Med. Inst. im. Sechenova, Moscow). *Gig. Sanit.* 33(1), 51-4(1968)(Russ). PMU-7 is a finely powd. dust contg. SiO₂ 30-5, Zn 15-20, Al₂O₃ 6-7, Fe₂O₃ 10-13, CaO 0-3, MgO 0.5-1.0, Mn 0.5, and Mo 0.02%. Without special care, there is danger from the dust during manuf. After intraperitoneal introduction, the LD₅₀ for mice is 833.5 mg./kg. Rats were exposed 4 hrs. daily, 6 days a week for 4 months, to an atm. contg. 5 mg./m.³. Reduced growth and erythrocyte counts and morphological changes in the lungs were observed.

John Howe Scott

62479a Poisoning with hydrogen sulfide in production of pinene mercaptan. Miroslav Bejsovec, Josef Budlovsky, and Borivoj Lehky (KUNZ Severoceskeho Kraje, Usti, Czech.). *Prac. Lek.* 19(9), 413-16(1967)(Czech). A case is described with a toxic impairment of the brain cells and capillaries and secondary edema of brain. It was followed by a slight non-uniform decrease in the intellectual capacity prevailing over 2 years, marked drop of spontaneous activity, marked disorder of the retention of fresh memory and of associative learning.

L. J. Urbanek

62480u Thermal decomposition products of poly(vinyl chloride). Toshio Tsuchiya and Kikuo Sumi (Div. Bldg. Res., Natl. Res. Council, Ottawa, Can.). *J. Appl. Chem.* (London) 17(12), 364-6(1967)(Eng). The toxic thermal decompn. products of poly(vinyl chloride) are detd. by pyrolysis followed by gas chromatographic anal. and their toxicities assessed by comparing the ratio of the concn. of a volatile product evolved when 1 g. of the original material is decompd. and the decompn. products are diffused in a vol. of 1 m.³ to its lethal (30 min.) concn. HCl is the main decompn. product followed by benzene which is always found in the product in both an inert atm. and air. CO and CO₂ are formed only in air and H₂, methane, ethane, ethylene, and PhMe are obtained in both He and air. The similarity of the volatile decompn. products found in the 2 different atms. suggests that the decompn. mechanism is nonoxidative and essentially thermal. HCl was the highest toxicity, being 3-10 times as great as that due to CO when poly(vinyl chloride) is decompd. in the presence of air.

CKJN

62481v Substantiation of the principles and methods for toxicological evaluation of volatile substances escaping from synthetic polymer products. I. M. Trakhtenberg, V. D. Bartenev, I. V. Savitskii, and V. E. Balashov (Kievsk. Med. Inst., Kiev). *Gig. Sanit.* 33(1), 97-9(1968)(Russ). The planning, design, and execution of expts. leading to toxicologic evaluation of industrial air contaminants such as formaldehyde, phenol, styrene, epichlorohydrin, amines, acrylates, cumene hydroperoxide, phthalic anhydride, sulfides, cyanides, fluorides, organochlorides, and organophosphorus compds. are discussed.

CPJR

62482w No abstr.

62483x Ultraviolet photolysis of sodium nitrate solutions in the laboratory and by sunlight. E. G. Gori, G. L. Petriconi, and H. M. Papez (Centro Nucl. Aerosoli, Rome). *Nature* 217(5125), 248-9(1968)(Eng). The photolysis of aq. NaNO₃ by artificial uv radiation and sunlight was studied. Artificially irradiated samples were analyzed for NO₂⁻ using the Griess reagent and, by titrating with MnO₄⁻, the amts. of near uv light absorbed were detd. The formation of NO₂⁻ was enhanced by the presence of Cl⁻ owing to the stabilization of the N oxides evolved by NOCl

THERMAL DECOMPOSITION PRODUCTS OF POLYVINYL CHLORIDE

By YOSHIO TSUCHIYA and KIKUO SUMI

When plastics are involved in a fire they may yield toxic decomposition products. Some quantitative data on the decomposition products of plastics are available in the literature, but it is difficult to assess the danger from the different amounts of various products because of the absence of a suitable method of evaluation. The authors have proposed a method of evaluation based on pyrolysis followed by gas chromatographic analysis and have used it to assess toxicity from various thermal decomposition products of polyvinyl chloride. Hydrogen chloride was found to be the main toxic decomposition product.

Introduction

The increasing use of plastics and other organic polymers raises the possibility that when involved in a fire they may yield toxic decomposition products in quantities sufficient to produce a dangerous atmosphere. Some quantitative results on the decomposition products of plastics are available in the literature, but it is difficult to compare data because of differences in experimental methods and differences in presentation of experimental data.

It is also difficult to assess the danger from the different amounts of various decomposition products because of the absence of a suitable method of evaluation. In view of the above factors, the authors believe that a need exists for a systematic study to provide quantitative results on the volatile decomposition products of a wide variety of plastics in both inert and oxidising atmospheres. A need also exists for a method of assessing danger from the different quantities of decomposition products. This investigation was carried out to meet these needs.

Polyvinyl chloride (PVC) is the plastics material that has probably received the most attention from fire authorities because of its relatively wide use and the possibility of its thermal decomposition leading to the formation of toxic gaseous products. This polymer was, therefore, selected for the present study.

Coleman & Thomas¹ determined the combustion products of PVC and other chlorinated plastics using a static system. The specimens were decomposed in a flask over a temperature range of 300 to 1000°. The ratio of plastics to air was varied by using different weights of sample, and the combustion products were analysed by conventional methods. Schriesheim² employed a similar method over a temperature range of 250 to 550° and analysed the products of combustion by a mass spectrometer and chemical methods. Stromberg *et al.*³ studied the mechanism of thermal decomposition of PVC in vacuum. The volatile products were analysed by mass spectrometry and found to consist almost entirely of hydrogen chloride and small proportions of benzene, toluene and other hydrocarbons. Gilbert & Kipling⁴ investigated the carbonisation of PVC and other vinyl polymers by decomposing the specimens, under vacuum, in an inert atmosphere and in air. After removal of hydrogen chloride the residue was decomposed and the products were analysed by gas chromatography.

In the present investigation the thermal decomposition products of PVC were determined, firstly, in an inert atmosphere and, secondly, in air. A flow system was adopted

instead of the static system used by other investigators,¹⁻³ because the decomposition conditions during an experiment can be more closely defined in a flow system than in a static system.

Experimental

Material

The PVC used in this study was a commercially available, general purpose resin in powder form. It did not contain any plasticiser.

Thermal decomposition

PVC was decomposed in a furnace through which inert gas or air was passed and the gaseous products were collected in a flask. The sample was weighed in a ceramic boat, to which a stainless steel wire and a piece of iron were attached, so that it could be moved inside a 19-mm diameter tube to the hot zone of the furnace by means of an external magnet. The furnace temperature was maintained at isothermal values of 350, 600 or 850°. Helium was used to provide an inert atmosphere in one series of experiments and air was used to provide an oxidising atmosphere in the other series. After some preliminary studies a gas flow rate of 450 cm³ per min was adopted. This corresponded to a mean linear velocity of about 160 cm per min. The sample weights selected for this study were 0.5 g in helium atmosphere and 0.5 and 0.25 g in air. The amount of air used during each experiment was slightly in excess of that required for complete combustion of 0.5 g of PVC to carbon dioxide, water and hydrogen chloride. The smaller weight of 0.25g was also used in an effort to examine the influence of effectively increasing air supply on the formation of decomposition products.

The higher boiling components of the decomposition products were collected in a U-tube filled with glass beads and maintained at 0°. The unreacted gas and the remainder of the volatile decomposition products were collected in a 3-litre flask that had been evacuated prior to the experiment. The sample was kept in the furnace until the gases filled the flask. Each experiment lasted about 8 min.

Analysis

Gas chromatography was the main method used in the analysis of decomposition products. As these were composed of widely differing materials, three chromatographic conditions had to be employed (two with a thermistor-type thermal conductivity cell detector, with different columns).

First a molecular sieve 5A (60- to 80-mesh) column of length 2 m and diameter $\frac{1}{8}$ in. (0.6 cm) was used with the

thermal conductivity detector at room temperature and a carrier gas (helium) flow rate of 60 cm³/min for the determination of hydrogen and carbon monoxide. Second, a silica gel (60- to 80-mesh) column of the same length and diameter as the molecular sieve column was used at 80° for the determination of carbon dioxide and chlorine. For quantitative analysis with the thermal conductivity detector the response of the detector was calibrated against its response to pure gases.

A hydrogen flame ionisation detector was used for the third condition, with another silica gel (60- to 80-mesh) column of length 6 ft (1.8 m) and diameter $\frac{1}{8}$ in. (0.3 cm) for determination of various hydrocarbons. A programmed temperature of 80° for 5 min., followed by a heating rate of 10 min. up to 300°, was used with a carrier gas (helium) flow rate of 30 cm³/min. Most of the peaks of the chromatograms obtained under this condition were identified by comparison with retention times of pure materials. Identification of some of the peaks was further confirmed by trapping the effluents, followed by analysis with a mass spectrometer. For quantitative analysis with the flame ionisation detector the response of the detector to n-butane was measured, and 'approximate substance specific correction factors' according to Kaiser's definition,⁵ were used to calculate the response of other components.

A calcium chloride trap was placed at the discharge end of the furnace tube to remove water vapour evolved. Some hydrogen chloride was absorbed by water vapour and was therefore trapped; the rest of the hydrogen chloride was determined along with carbon dioxide by a gravimetric method in which ascarite was used. The amount of hydrogen chloride not absorbed in water vapour was determined by subtracting the amount of carbon dioxide previously determined by gas chromatography.

In an effort to determine chlorine, if present, a sensitive colorimetric detector tube (Kitagawa) was used. This detector is recommended for concentrations of 1 to 40 ppm.

Results and discussion

The results of the determination of the volatile thermal decomposition products of PVC in an inert atmosphere and in air are given in Table I. They are reported as percentage by weight of original polymer, and are based on means of two or more repeat tests.

The main decomposition product of PVC was hydrogen chloride. Almost all the chlorine in PVC was converted to hydrogen chloride. The amount of hydrogen chloride produced in an inert atmosphere approached the theoretical value

expected from PVC. The amount determined in an oxidising atmosphere was slightly lower, because water vapour produced in an atmosphere of air absorbed some of the hydrogen chloride. The amount of hydrogen chloride absorbed in water was intentionally neglected and the lower value reported because the toxicity of hydrogen chloride produced at a fire is primarily due to the gas. The amount absorbed in the water would condense on cool surfaces and play a comparatively minor role. If this amount had been included, the results for hydrogen chloride would have approached the theoretical value because no appreciable amounts of other chlorine compounds were found in the decomposition products. Neither chlorine nor phosgene was detected. The minimum amount of chlorine that could have been determined in the present investigation was 0.003 wt.-% of the original polymer.

The results for the two different sample weights were very similar. At the lower sample/air ratio, slightly more carbon dioxide was produced at the expense of hydrocarbons. The highest carbon monoxide concentration was found at 600°; the amount was less at 850° because of further oxidation to carbon dioxide.

Benzene was always found in the product in both an inert atmosphere and air. The formation of benzene and other aromatics can be explained on the basis of the removal of hydrogen chloride from the polymer, producing a polyene system followed by the formation of stable six-membered rings.³

The similarity of the volatile decomposition products of PVC found in two different atmospheres suggests that the decomposition mechanism is non-oxidative and essentially thermal. The only oxidation products found were carbon monoxide and carbon dioxide. Other oxidation products such as acids, aldehydes, alcohols, ketones, etc. were not found. This observation is in agreement with the author's experience with the decomposition of polyethylene in air.

Efforts were made to assess the danger that might arise from various quantities of thermal decomposition products of PVC as determined in the present investigation. A literature search was undertaken to find data on relative toxicity of different materials. The most detail available is on maximum allowable concentrations of gases and vapours at which no adverse effect is expected.⁶⁻⁸ Some information is available on higher levels of concentrations such as those fatal to animals in a short time and the authors believe that such data would be more applicable to fire situations than the maximum allowable concentrations.

Difficulties were experienced in finding consistent data on

TABLE I
Decomposition products of PVC

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Temp. of decomp., °C		350	600	850	350	600	850
Wt of sample, g		0.5	0.5	0.5	0.5	0.5	0.5
Atmosphere		He	He	He	Air	Air	Air
Decomposition products, wt.-% sample	HCl	53.2	55.5	57.9	47.2	46.0	40.6
	CO	—	—	—	1.0	35.6	16.6
	CO ₂	—	—	—	1.7	40.8	54.8
	H ₂	—	0.06	0.47	—	0.16	0.50
	CH ₄	—	1.0	3.2	—	1.7	3.4
	C ₂ H ₆	—	0.60	0.32	—	0.14	0.06
	C ₂ H ₄	—	0.52	2.5	—	0.63	1.3
	Benzene	5.9	5.6	5.9	5.4	4.7	3.1
	Toluene	0.05	0.67	0.87	—	0.22	0.89
	Residue	37.4	6.3	5.1	40.2	2.4	—

TABLE II
Toxicity from decomposition products of PVC

Temp. of decomp., °C	350	600	850	350	600	850	350	600	8
Wt of sample, g	0.5	0.5	0.5	0.5	0.5	0.5	0.25	0.25	0
Atmosphere	He	He	He	Air	Air	Air	Air	Air	A
Toxicity, $t = \frac{c_0}{c_t}$	HCl	0.33	0.34	0.36	0.29	0.29	0.25	0.30	0
	CO	—	—	—	0.002	0.07	0.03	0.002	0
	CO ₂	—	—	—	0.00004	0.001	0.001	0.00006	0
	C ₆ H ₆	0.003	0.003	0.003	0.003	0.002	0.001	0.002	0
Total toxicity		0.33	0.34	0.36	0.29	0.36	0.28	0.30	0

the relative toxicity of the main decomposition products of PVC for very short exposures. Data on concentrations of gases and vapours considered fatal to man in a 30-min exposure (c_t) were assembled. Toxicity (t) due to a gaseous or volatile product was assumed to be proportional to its concentration and to its relative toxicity (t_r) i.e., $t \propto ct_r$. Relative

toxicity was defined as: $t_r = \frac{1}{c_t}$.

The toxicity of a decomposition product, based on both the nature of the material and the quantity evolved, then becomes:

$$t \propto \frac{c}{c_t}$$

By comparing values of c/c_t for different decomposition products evolved under one set of conditions, toxicity from each product could be assessed. In order to present data on toxicity in a consistent manner the authors suggest using the equation:

$$t = \frac{c_0}{c_t}$$

where c_0 is the concentration of a volatile or gaseous product evolved when one gram of original material is decomposed and the decomposition products are diffused in a volume of 1 m³, and c_t is the concentration of gases lethal to man after 30 min.

Toxicity, based on the above equation, was determined for the analytical results obtained in the current investigation and presented in Table II.

The main decomposition product of PVC was hydrogen chloride. The toxicity due to that product was found to be three to ten times as great as that due to carbon monoxide when PVC was decomposed in the presence of air. Even if it were possible to convert all the carbon of PVC to carbon monoxide the degree of toxicity (based on the present method of evaluation) due to hydrogen chloride would be twice as great as that due to carbon monoxide.

The toxicity due to the decomposition products of different polymers can also be evaluated if, as a first approximation, synergism is neglected and it is assumed that the combined effect of toxicity is additive. The data for PVC are also given in Table II. The toxicity due to decomposition under different

experimental conditions could also be studied using method of evaluation by varying temperature, sample ratio, etc.

The authors realise the limitations of the proposed method of evaluation. Toxicities are not necessarily additive, and mechanisms of the toxicity for hydrogen chloride and carbon monoxide are quite different. The most serious effect of hydrogen chloride is on the eyes or respiratory tract. Toxic effect of carbon monoxide is due primarily to its affinity for haemoglobin, and this could lead to damage of the brain. Synergistic effects between different conditions, e.g., heat, carbon monoxide concentration, and oxygen depletion, were neglected because the present state of knowledge on this subject precludes consideration of a simple formula. In spite of these limitations, the proposed methods of evaluation should be of value, especially in the design of animal experiments to obtain data on toxicity.

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