THE FORMALDEHYDE PROBLEM IN WOOD-BASED PRODUCTS--

AN ANNOTATED BIBLIOGRAPHY

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ABSTRACT

Urea-formaldehyde-type adhesives have the inherent characterzistic of giving off free formaldehyde under some conditions of use. The vapor can build up to concentrations which can be a nuisance, uncomfortable, or an actual health hazard. The "formaldehyde problem" is reviewed, from literature sources, in five respects: Oriqins, Analytical, Control and Removal, Toxicology, and Odor and (general methods of) Odor Control. Correlation between the citations in each section, and between the sections, is provided by appropriate annotation. The report is current to January 1977.

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INTRODUCTION

This Laboratory is increasingly involved with the development of adhesive–bonded, wood-based fiber and particle–panel materials.[2] Questions frequently arise with respect to the liberation of formaldehyde from such materials. Condensation polymers of formaldehyde are used as industrial woodworking adhesives. One of the more commonly used resins of this type is urea–formaldehyde (UF), which finds extensive use in the production of particleboard and hardwood plywood. Unfortunately, these adhesives have the inherent characteristic of giving off free formaldehyde (HCHO) during their use in the producing plant, and during storage or use of the resulting glued–wood products. The extensive utilization of such panel board products for interior construction of habitable space has led to what is called the "formaldehyde problem"– –a buildup of the vapor to concentrations that are a nuisance, uncomfortable, or an actual health hazard.

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[1] Maintained at Madison, Wisconsin, in cooperation with the University of Wisconsin.

[2] American Society for Testing and Materials, 1974. Standard definitions of terms relating to wood–base fiber and particle–panel materials. ASTM Desig. D 1554–67. ASTM, Philadelphia, Pa.

Earlier reviews (A18 , A20, A25) of the formaldehyde problem are no longer available, and that which still is (A15) included literature to about 1968-1969. The present review is an extension and updating with broadened coverage. It is divided into five topical sections: A. Origins, B. Analytical, C. Control and Removal, D. Toxicology, and E. Odor and Odor Control. Corresponding literature citations, serially numbered, begin on page 7 of this report. The published literature was reviewed principally through Chemical Abstracts[3] for the period beginning with issue No. 1, January 1969, to issue No. 4, January 24, 1977. Supplementary use was made of Forestry Abstracts,[4] and of "Toxline"[5] for Section D. Toxicology, An additional and important source of information has been released by National Institute for Occupational Safety and Health.[6]

The annotations accompanying each citation are not verbatim copy of the published abstract; rather, an attempt has been made to give a concise and descriptive summary from the abstract. In many cases, the original report was obtained and read, permitting the notations to be specific and/or allowing the author to make correlating commentary between citations and the general sections. It is hoped that the result is a rapidly readable analytical summary of the formaldehyde problem as it has been presented in published literature,

For the majority of references herein, the citation in Chemical Abstracts[3] has been included, making it possible for the reader to consult the original abstract,

During editing, several very recent, pertinent reports were found. These new citations appear at the beginning of the bibliography of the appropriate topical sections.

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[3] American Chemical Society. Current, Chemical Abstracts. Publ. weekly, two volumes per year. Am, Chem. Soc., Chem, Abs. Serv., Columbus, Ohio.

[4] Commonwealth Forestry Bureau. Current, Forestry Abstracts. Issued monthly, Oxford, England. Commonwealth Agric. Bureau , Farnham Royal, Slough, SL2 3BN, U.K.

[5] National Library of Medicine. Current. "Toxline." Remote-access Retrieval Service, NLM, Bethesda, Md. A computer stored information system for toxicological information.

[6] U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health. 1976, Criteria for a Recommended Standard......Occupational Exposure to Formaldehyde. HEW Publication No. (NIOSH) 77-126. U.S. Dept. HEW, Public Health Service, Center for Disease Control, NIOSH, Rockville, Md.

DISCUSSION

Section A. Origins of Formaldehyde Problem

The literature is replete with discussions of and solutions for the odor of formaldehyde (HCHO) released from particleboard. A broad presentation of the subject was given by Gillespie (A15). Earlier, Neusser and Zentner (A23) published a comprehensive discussion of almost all phases of the problem. And Plath (A24) reported a series of experimental investigations of the parameters of particleboard manufacture as did Roffael (B5) and Hse (A9) more recently. The problem is one faced also by the textile industry in developing crease-resistant cloth. Inasmuch as the chemistry of formaldehyde-type bonding resins is at the root of the problem, the review by Kelly (A17) is pertinent. The accelerated-aging studies by Troughton (A21) contribute further to understanding the chemistry of this type of resin binder insofar as the emission of HCHO can continue from the finished products.

Unfortunately for an easy solution, the problem is intrinsic with the product, And the solutions proposed are often more suitable for application during manufacture than to the product after manufacture. In other words, the ultimate user is not likely to be able to eliminate the odor as readily or conveniently as is the manufacturer.

Section B. Analytical Methods

A factor which may loom large in the analysis for formaldehyde is whether more stringent exposure conditions will be mandated by future Occupational Safety and Health Administration (OSHA) regulations. The essentially ubiquitous exposure of the public to formaldehyde, and the increasing recognition of its toxicity (Section D) will require greater analytical sensitivity with accompanying accuracy and precision. The situation has been recognized already by industry to the extent in one case (B32) that the plant limit was established at an air concentration lower than the officially (D22) recognized threshhold level value.

Few of the methods reviewed are particularly suitable for rapid process control or for onsite tests in conjunction with air pollution of habitable space. In the latter case, little use appears to have been made of commercially available detector tube systems; sensitivity may possibly be too poor, considering the very low level at which formaldehyde can be a human irritant. (See also B43.) Further application of the purpald color test (B19) in the testing of particleboard for potential release of HCHO has not been found in the literature.

The rapidly increasing use of particleboard materials in domestic applications (e.g., residential housing) may well force the issue in two respects: Better analytical methods to protect the production worker (OSHA regulations) and more stringent control of manufacturing parameters to avoid postproduction liberation of formaldehyde into habitable space such as was the case in Danish (A3) and other European housing (A23).

Section C. Control and Removal of Formaldehyde

The control and removal of formaldehyde may be regarded conveniently in two respects: (1) During manufacture and (2) afterwards.

The annotations for each reference are also classified in terms of the type of control method represented: Adhesive; Adsorbent; Coating; and Ventilation, Thus, adhesive control will be a parameter largely under control of the manufacturer. On the other hand, coatings and ventilation methods could be used by either user or manufacturer. Adsorbents could be largely a way for the user to deal with the odor. Actually, elimination of the formaldehyde odor is not readily accomplished conveniently, Many qualitative solutions have been proposed, but there is a notable lack of quantitative information that permits an effective solution at "the end of the line"--i.e., after the material has been installed and found to be actively emitting formaldehyde at unacceptable rates.

This section deals with published methods specifically developed for application to formaldehyde. General methods for odor control are collected in Section E.

The application of ultraviolet radiation for the purpose of generating ozone whereby formaldehyde is oxidized to less harmful or annoying materials has been utilized industrially on a large scale (E15). But no citations were found where the procedure was applied on a small scale with low-intensity UV lamps, There is, however, some confusion in the literature with respect to the effectiveness of ozone in eliminating odors in general (E6, E7), while its hazard for human exposure is recognized clearly (D22, E6, E16). Because of the lack, therefore, of experimental data for such small-scale applications the use of ozone in this fashion for combating formaldehyde odor cannot be recommended, even though the statement is made (E7) that ozone is self-policing--i.e., the concentration at which it is immediately noticeable by its odor is below harmful levels. Unfortunately, this statement has a built-in hazard, namely, the well recognized potential for human odor sensation to be desensitized, hence possibly masking harmful substances.

Section D. Toxicology of Formaldehyde

The potential--if not actual — toxic effects of formaldehyde on the human body are clearly pointed out in general (D4), and in more specific (D5) terms. And earlier, in a very practical approach to evaluating formaldehyde as an industrial hazard, Freeman and Grendon (B32) presented experimental data to illustrate a probable cause-and-effectrelation in its effect upon human performance. They recommended lower environmental levels for plant employees, At present the official limit is 3 parts per million (ppm) (D22). But the NIOSH[6] recommended standard defines "occupational exposure" as a concentration of HCHO in air in excess of 0.5 ppm for a 30-minute sampling period, with maximum exposure to 1 ppm for any 30-minute period.

One of the most significant aspects of chemical toxicity is that related to human health effects, and, more particularly, environmental chemicals as potential hazards to reproduction. This subject is especially well presented in Chapter 10 of D4. The seriousness of chemical hazards is emphasized by a list of 13 events and processes that are directly involved in reproduction.

A newly born infant may be unusually susceptible to chemicals as for example if its immature metabolic systems are unable to cope with foreign substances (at concentration levels which have been established for a full-grown human adult[7]). Further, all of the 13 reproductive processes (D4) have been demonstrated in experimental animals to be altered by exposure to certain environmental agents, each process having its own level (concentration) of susceptibility to abnormality. The reproductive process is most vulnerable to mutagenesis and teratogenesis; aldehydes have been implicated in the former already (D4).

The significance of possible detrimental effects from exposure to formaldehyde on the broad scale that appears now to be true should not be dismissed, especially as regards the increased use of adhesive-bonded and reconstituted wood-base materials. The use of such in home construction could result in exposure to people of all ages. The situtation has been more clearly defined with the release of the NIOSH criteria document[6] on occupational exposure to formaldehyde. And with the responsibility of EPA for air quality within and outside the home, this Federal agency may be expected to be interested in the problem in large degree.[8]

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[7] This author's added comment.

[8] Studies referred to, D4 and D5, were requested and funded by the Environmental Protection Agency.

Section E. Odor and Odor Control

Frequently, it is convenient to have access to information on a broad as well as specific basis. This section provides sources for the former, and ones which are generally considered authoritative in industrial practice. Sources from both the American Society for Beating, Refrigerating, and Airconditioning Engineers (ASHRAE) (E5, e.g.) and the American Society for Testing and Materials (ASTM)(E8) are updated yearly or periodically as necessary. An extensive bibliography is included with ASHRAE chapters, permitting access to the original published literature.

Recent references added during the publication process are included at the beginning of each appropriate section, and are identified with a double-letter system rather than with the letter-number system.

FORMALDEHYDE BIBLIOGRAPHY

Section A. Origins of Formaldehyde Problem

Aa. Kelly, Myron W.
1977. Critical literature review of relationships between processing parameters and physical properties of particleboard. USDA FS General Technical Report FPL-10. Forest Products Laboratory, Madison, Wis.

A paper very aptly described by its title, The author includes strength and moisture and dimensional properties. Among the parameters reviewed are resin efficiency, type, and level, furnish, and pressing conditions. The release of formaldehyde is influenced, however, by many factors, with no single manufacturing parameter responsible or controlling. A particular need for effective study of the formaldehyde problem is a quantitative analytical procedure for the low concentrations of formaldehyde encountered (See B32, B33).

Comment: The discussion of HCHO release is such as to be of more interest to the manufacturer and/or the particleboard researcher. The discussion is an extension of the author's previous publication (A17) on the subject, at which time the chemistry was presented in detail.

Ab. Roffael, E.
1976. Effect of formaldehyde content on the reactivity of urea-formaldehyde resins and formaldehyde release from UF-bonded particleboard. Holz Roh-Werkst. 34(10):385-390.

This latest report cited here confirms the relationship between the ratio of formaldehyde and urea in determining the release of HCHO from UF-bonded particleboard. In addition, formaldehyde content above a certain range appears to influence strength properties negatively. See also A9, A17, B32.

A1. Roffael, E.
1976. The importance of components of bark for their use in particleboard. Part I. Effect of components on the formaldehyde release of bark boards, Holzforschuhg 30(1):9-14. Chem. Abs. 84:166526 (Ger.).

Using pine, spruce, and beech bark to make particleboard, the author observed a species effect insofar as the amount of formaldehyde (HCHO) released by each board was concerned. Furthermore, extractives from spruce bark were more reactive to HCHO than were those from pine and beech barks. The results were compared with board made from pine wood chips.

Comment: In the use of whole wood to make particleboard, oak was found to liberate more formaldehyde than spruce (A13) ; but oak and pine behaved similarly to each other (C2).

A2. (a) Takahashi, T., M, Kitazawa, and T. Anazawa
1975. Effects of manufacturing conditions on formaldehyde liberation from particleboards. Rinsan Shikenjo Geppo (8) :9–13. Chem. Abs. 84:61579 (Jap.).

(b) 1975. Formaldehyde liberation from particleboards. Rinsan Shikenjo Geppo (283) :9–13. Chem. Abs, 84:61581 (Jap.).

Manufacturing parameters--particle moisture content, pressing temperature and time, and storage time (aging of the board)--affected the release of formaldehyde. The use of urea and/or melamine acted as formaldehyde scavengers without affecting mechanical properties.

Comment: This and the citations C4, C5 appear to be a coordinated study of the means for reducing the liberation of formaldehyde from particleboard through control of experimental parameters during manufacture, The same or similar approaches have been used by others; see A7, A13, A16, A17, A24.

A3. Andersen, Ib, Gunnar R. Lundqvist, and Lars Molhave
1975, Indoor air pollution due to chipboard used as a construction material. Atmos. Environ. 9(12):1121–1127. Chem. Abs, 84:126156.

A condensation, in English, of the three Danish language publications (A4, A5, A6) by the same authors,

Comments: See also B1, B30 in which measurements also showed that increased ambient temperature and board moisture content raised the level of evolved formaldehyde.

A4l Andersen, Ib, Gunnar K. Lundqvist, and Lars Molhave
1974, Formaldehyde in the atmosphere in Danish homes. Ugeskr. Laeg. 136(38):2133–2139, Chem. Abs. 82–34672 (Dan.).

One hundred measurements of the formaldehyde content in 25 rooms in 23 one-family houses (mostly new or recent) showed an indoor average of 0.62 mg/m^3 air, with a range of 0.08 to 2.24 mg/m^3 (1.2 mg/m^3 = 1 part per million, ppm). In 17 rooms, the value was higher than that desirable for long-term exposure (0.40 mg/m^3). In these circumstances, the authors presume that the inhabitants will experience upper respiratory tract effects such as lowered mucociliary rate of transport, lowered threshold for sense of smell, increased airway resistance, and irritation of the mucosa in the nose and conjunctiva.

Comment: This is the only report found to deal directly with the problem of formaldehyde odor arising in existing dwellings from use of particleboard. The physiological effects are not uncommon. See also All and Section D.

A5. Andersen, Ib, Gunnar R. Lundqvist, and Lars Molhave 1974. Liberation of formaldehyde from particleboard under controlled conditions in a climate chamber, Ugeskr. Laeg. 136(38):2140-2145. Chem. Abs, 82:21259 (Dan.).

Experimental work relevant to reference A4. Further confirmation is given of the fact that the evolution of formaldehyde increases with both higher temperature and humidity.

A6. Andersen, Ib, Gunnar R. Lundqvist, and Lars Molhave 1974. Liberation of formaldehyde from particleboard: Mathematical model, Ugeskr. Laeg. 136(38):2145-2150, Chem. Abs. 82:21260 (Dan.).

A mathematical model was derived based on experimental measurements in a climate chamber. By introducing a correction factor the model was adapted to actual dwellings, permitting estimation of an anticipated value for the equilibrium concentration of formaldehyde for a given room.

A7. Peterson, H., W, Reuther, W. Eisele, and O. Wittmann 1974. Formaldehyde liberation during particleboard production with urea-formaldehyde adhesives. Part III. Effect of hardener type, amount of hardener, and formaldehyde binding agents. Holz Roh- Werkst. 32(10) :4O2-410. Chem. Abs. 82:126805 (Ger.).

A number of ammonium and metal salts were tried as hardeners for their effect upon formaldehyde liberation during manufacture. Increasing amounts of the ammonium salts reduced the liberation, NH_4Cl being most effective.

Several nitrogen-containing compounds, as well as NE_3 and urea, were tested for their scavenging action on formaldehyde. The type and amount of hardener are also decisive factors, in addition to pressing conditions, in the liberation of formaldehyde during manufacture and storage.

Comment: See also references A13 and A16 for previous publications, and references A9, A24, and B5 for similar investigations of the relationship of manufacturing parameters to formaldehyde liberation.

A8. Kravchenko, T. I., K. I. Stankevich, E. F. Malygina, and T. G. Zakharova
197.4, Migration of formaldehyde from wood sheets. Gig. Sanit. (5):19-22. Chem. Abs. 81:123227 (Russ.).

The evolution of formaldehyde from construction-type particleboard is approximately ten times greater if the board is made from sawdust than from wood chips. The rate of evolution was considerably less after 6 months' storage. See also reference A26 with respect to groundwood use.

A9. (a) Hse, C. Y.
1974. Characteristics of urea-formaldehyde resins as related to glue bond quality of southern pine particleboard. Mokuzai Gakkaishi 20(10):483-490. Chem. Abs. 82:45434.

(b) 1974. Reaction pH of urea-formaldehyde resins as related to strength properties of southern pine particleboard. Mokuzai Gakkaishi 20(10):491-493, Chem. Abs. 82:45435.

(c) 1974. Reaction catalysts of urea-formaldehyde resin, as related to strength properties of southern pine particleboard. Nokuzai Gakkaishi 20(11):538-540. Chem. Abs. 82:60235.

Together, these three papers present the relationship between the parameters of resin (urea-HCHO) formulation and the strength properties of particleboard made from them. Of particular interest here is that free formaldehyde content (of the resins) was linearly and positively correlated with the four measured strength properties: Internal bond, screw withdrawal, modulus of elasticity, and modulus of rupture. The free formaldehyde content was significantly increased by the HCHO/urea ratio in the range of 1.7 to 1.9, a factor of importance in the odor problem. The author's hypothesis is that free HCHO promotes liberation of acid from the reaction catalyst during cure, thus promoting polymerization additionally. Under conditions of low free formaldehyde, cure rate is low and poor bonding results.

Comment: The three papers are in English.

A10. Grigoreva, M. N., and N. G. Shplet
1974. Use of a urea plastic foam sealant in enclosing structures. Tr. Leningr. Sanit.-Gig. Med. Inst. (105):177-178. Chem. Abs. 84:140033. (Russ.).

The use of foamed resin (e.g., urea-formaldehyde) building panels poses a potential odor problem. The authors recommend a test for possible evolution of HCHO before use.

All. Matsumoto, T.
1974. Concentration of formaldehyde released from plywood in an environmental test room. Ringyo Shikenjo Kenkyu Hokoku (262):41-58. Chem. Abs. 82.:60159. (Jap.).

The information presented supplements that reviewed earlier (<u>A4</u>, <u>A5</u>, <u>A6</u>). Confirmation is given to the fact that temperature and humidity both affect HCHO odor level (<u>A5</u>).

A12. Temkina, R. Z., M. M. Svitkina, and G. G. Yuclina
1974. Standard for resin KS-68. Derevoobrab. Promst. (9):3-5. Chem. Abs. 82:74039 (Russ.).

Standards are recommended for three grades of a urea-. formaldehyde binder used in the manufacture of particleboard and plywood. The free formaldehyde concentration is set at $\leq$0.3 to 1.0 percent,

A13. Peterson, H., W. Reuther, W. Eisele, and O. Wittmann
1973. Further investigations on the formaldehyde liberation during particleboard production with urea formaldehyde adhesives. Part IT. Effect of resin quantity, pressing time, and temperature. Holz Roh- Werkst. 31(12):463-469. Chem. Abs. 80:147103 (Ger.).

The parameters in the title have a decisive effect on the liberation of formaldehyde during production and storage of particleboard, More formaldehyde is liberated from oak particles than from spruce. Moisture content is also a parameter affecting the evolution of formaldehyde.

Comment: The paper deals primarily with these parameters insofar as they are controllable during manufacture. However, the application of particleboard in consumer situations is effectively similar to storage, especially if the particleboard is put into use too soon after manufacture. See also A28.

A14. Winkler, Hans Dieter, and Klaus Welzel
1972. Formaldehyde emissions from pressboard production. Wasser, Luft Betr. 6(7):213–215. Chem. Abs. 77:143548 (Ger.).

The source of, testing for, and the possibilities of minimizing the emission of formaldehyde are discussed in respect to various phases of the industrial processing plant.

Al5. Gillespie, R. H.
1972. That panel odor--when it may occur--what you can do about it. No. 72–015. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wis. 7 p.

The edited version of a 1969 publication (A20) having the same title, The author discusses concisely sources of the problem, the question of whether formaldehyde is a health hazard, the roles of the adhesive manufacturer, the panel manufacturer, and the wholesaler and retailer in controlling the parameters giving rise to formaldehyde evolution. Finally, the end–use location, namely with the homeowner and businessman, is discussed principally in respect to what can be done to alleviate a situation wherein the odor of formaldehyde is objectionable.

Comment: Though based on two older literature surveys (A20 and A25), the information provided remains valid. References cited have not been superseded altogether by more recent publications cited in the present survey.

Al6. Peterson, H., W. Reuther, W. Eisele, and O. Wittmann
1972. Investigations on the formaldehyde liberation during the manufacture of particleboard with urea formaldehyde adhesives. Holz Roh–Werkst. 30(11): 429–436. Chem. Abs. 78:86203. (Ger.).

The first in a series of three papers (see A7 and A13) having the same main title and authors. Eight major factors are listed as influencing the liberation of formaldehyde during manufacture and storage:

(1) Urea–formaldehyde molar ratio of the adhesive.
(2) Free formaldehyde content in the adhesive.
(3) Moisture content of the glued wood chips.
(4) Amount of hardener.
(5) Type of hardener (i.e., composition of mixture).
(6) Amount of resin applied,
(7) Compression temperature.
(8) Compression time.

The paper reports data with respect to items (1) , (2), and (3) above. Thus, particleboard pressed from chips containing higher moisture content (e.g., 15 to 16 pct) liberated more (about 50 pct) formaldehyde than if the moisture content was low (10 pct). The same general relationship applied during storage (postmanufacture liberation) as well. A method was developed for measuring formaldehyde liberated during and after pressing, Analysis for HCHO was by the sodium sulfite method (A29, B33).

A17. Kelly, M, W.
1970. Formaldehyde odor and release in particleboard,
Proc. 4th WSU Particleboard Symp.
Wash. State Univ., Pullman, Wash. p. 137–149.

Three aspects of the formaldehyde problem are discussed:

(1) Chemistry of adhesives and the curing process;
(2) Causes of formaldehyde release; and
(3) Formaldehyde analysis (see section B--
for example, B19 and B33).

The degradation of methylol end groups, which are not completely reacted during the curing process in the hot press, is believed to be the primary source of formaldehyde released from urea-formaldehyde-type adhesives. A more immediate source during manufacture and for a period thereafter, is the free formaldehyde added to enhance the curing rate. Adequate control of the many manufacturing processes and parameters can alleviate the problem.

A18. Forest Products Laboratory
1969. Eliminating odor from urea–resin–bonded plywood
and particleboard: Glues and Glued Products Project.
U.S.D.A. Forest Service, Forest Products Laboratory,
Madison, Wis. 15 p., 39 refs.

An abstract bibliography containing references up to 1968.

Comment: The present survey is an extension of this older one, but now arranged on the basis of topics (five) and in chronological order beginning with the most recent citation in each group. The above is no longer available for distribution from the Forest Products Laboratory.

A19. Canadian Department of Fisheries and Forestry
1969. Research News, 12(2 March-April): 4. Can. Dept. Fisheries and Forestry, Ottawa, Ont.

A concise discussion of the formaldehyde-particleboard problem prepared for public relations purposes. Several typical uses fox particleboard are labeled as "misuse" because the material is used without any sealing of the surface to reduce liberation of formaldehyde.

Comment: This writer disagrees with the statement that [formaldehyde] is not poisonous. That may be so in the sense of not being deadly, but the dictionary definition of a poison includes the possibility of producing an injurious effect as well. That formaldehyde can be injurious to the human body is detailed in Section D).

A20. Gillespie, R. H.
1969. That panel odor--what you can do about it. U.S.D.A., Forest Service, Forest Products Laboratory, Madison, Wis. 10 p., 17 refs.

Comment: See A15 above for edited version.

A21. Troughton, G. E.
1969. Accelerated aging of glue-wood bonds. Wood Sci. l(3):172-176. Chem. Abs. 70:107666.

Mild acid conditions were used to accelerate the hydrolysis of glue-wood bonds, the course of the reactions being followed by the formaldehyde liberated (a colorimetric method of analysis for formaldehyde was used). Half-lives calculated for the acid-hydrolysis reactions provided an index (for estimating glue-wood bond durability) that was in good agreement with service life. The urea-formaldehyde type had the lowest durability index.

Comment: The research very definitely pinpoints a source of formaldehyde liberated from particleboard. Even if all free formaldehyde, added to enhance the cure of the adhesive, could be removed, there remains a certain number of unreacted methylol end groups (see A17) which are subject to acid hydrolysis. Furthermore, such release of formaldehyde from cured urea-formaldehyde resins is increased by heat and moisture. As will be seen in Section C, any procedure which reduces the absorption of moisture by particleboard will tend to reduce the rate of this hydrolysis action.

A22. Pushkina, I. K.
1969. Industrial hygiene in the production of woodchip particleboards, Gig. Vop. Proizvod. Primen, Polim. Mater. 38-46. Chem. Abs. 75:143692 (Russ.).

A discussion of the health hazards associated with various stages of particleboard production. Remedies are proposed for reducing formaldehyde in the plant atmosphere as well as its release from the finished products. Unsafe working conditions were recognized by the fact that the concentration of formaldehyde was three to four times the permitted maximum.

A23. Neusser, H., and M. Zentner
1968. Causes and the control of formaldehyde odor from wood-based building materials, especially particleboards, Holzforsch. Holzverwert. 20(5):101-112. Chem. Abs. 70:88985 (Ger.).

The formaldehyde problem is covered in almost all its aspects, as shown by the following list of section subtitles:
(1) The odor of formaldehyde and its effect upon people,
(2) The importance of ventilation in a room.
(3) Odor and irritation thresholds for formaldehyde in room air.
(4) Free and releasable formaldehyde from urea resins.
(5) Formaldehyde emitted during the hot pressing of particleboards.
(6) The formaldehyde content of particleboards following pressing.
(7) Emission over extended periods of time.
(8) Studies on industrially manufactured particleboards.
(9) Cases of complaints and their elimination.
(10) Summary.
(11) Bibliography--37 citations.

Much quantitative information is given in some sections; two, (2) and (3) above, are particularly important to the practical problem of alleviating the odor from installed boards. A footnote in section (4) gives definitions for four "kinds" of formaldehyde, based on the time at which the formaldehyde is determined during the course of manufacture. Section (7) compares the emission of formaldehyde from board surfaces versus from the edges.

A24. (a) Plath, L.
1968. Tests on formaldehyde liberation from particleboards. VI. Test series on formaldehyde liberation from industrial particleboards. Holz Roh-Werkst. 26(11):409-413 (Ger.).

(b) 1968. Tests on formaldehyde liberation from particleboards. V. The influence of curing acceleration and aging period on formaldehyde liberation, Holz Roh-Werkst, 26(4):125-128. Chem. Abs. 69:88118 (Ger.).

(c) 1967. Tests on formaldehyde liberation from particleboards. IV. Effect of moisture content in chip mat on formaldehyde liberation. Holz Roh-Werkst. 25(6):231-238 (Ger.).

(d) 1967. Tests on formaldehyde liberation from particleboards. 111. Effect of hardeners on formaldehyde liberation. Holz Roh-Werkst. 25(5):169-173. Chem. Abs. 67:83121 (Ger.).

(e) 1967. Tests on formaldehyde liberation from particleboards. II. The influence of pressing time and temperature on formaldehyde liberation. Holz Roh-Werkst. 25(2):63-68. Chem. Abs. 67:23052 (Ger.).

A series of six papers dealing with parameters relevant to the industrial production of particleboard. (See B41, the first paper in the series, for details of Plath's analytical procedure for determining the formaldehyde liberated from particleboard.) As the main title implies, the amount of formaldehyde emitted was the principal concern as a function of the experimental parameters. In paper (e), the author finds that formaldehyde liberation is largely dependent upon the composition and amount of hardener. And because board quality is very sensitive to hardener composition, the possibility of reducing formaldehyde liberation is limited.

Comment: In Section C. Control Methods, more recent efforts are being directed towards altering the composition of the adhesive, the addition of materials capable of binding the formaldehyde irreversibly, and the development of coatings which slow the release of formaldehyde.

A25. U.S.D.A. Forest Service, Forest Products Laboratory, Library
1968. Literature on the problem of formaldehyde odor from urea resins. Unpublished bibliography. Library U.S.D.A. Forest Service, Forest Products Laboratory, Madison, Wis. April. 3 p.

A bibliography by title and source only. It covers the period 1953-1968 (a single reference is dated 1942), with the majority in the 1960's. Included are citations to textiles because of the relationship of urea formaldehyde resins in the production of wrinkle-, or crease-proof fabrics. (See p. 94 of the section "Use" in A27.)

A26. Sukovatov, V. I., T. Galitsina, A. I. Isaev, and V. V. Kharchenko
1968. Evolution of phenol and formaldehyde from articles made of molded wood chips. Tr. Nauchno-Issled. Inst. Stroit. Ugol. Gornorud. Predpr. No. 5, 311-320. Chem. Abs. 74:130082 (Russ.).

Ground wood was used with a phenolic-type binder which liberated both phenol and formaldehyde. During the first 6 months after manufacture, both compounds were present at concentrations which exceeded permissible limits.

Coment: See also A8 where particle size was reported to affect the evolution of formaldehyde.

A27. Walker, J. F.
1966. Formaldehyde. Kirk-Othmer Encyclopedia of Chemical Technology. 2d ed., V. 10, p. 77. Interscience Publ., John Wiley and Sons, N.Y.

A summary of the chemical and physical properties of all forms of formaldehyde (gas, solution, and polymeric), including major reactions and derivatives. Manufacture, analysis, health and safety factors, and use are covered.

Comment: Considerably more information is to be found in the book by Walker (A29), but the above may be considered a very convenient and useful refresher. This author believes, however, that, in the section "Health and Safety Factors," permissible concentrations in air for all human exposures are seriously outdated. This will be appreciated from the citations given in Section D. Toxicology.

A28. Deppe, H. J., and K. Ernst
1965. On reducing compacting time in chipboard manufacture.
Holz Roh-Werkst. 23(11):441-445. (Ger.).

Pressing time (and temperature) were investigated experimentally from the standpoint of economic commercial production of particleboard. It is obvious, however, that any tendency to produce undercured particleboard will result in a product that will probably exhibit high evolution of formaldehyde in use.

Comment: These conclusions were later confirmed by Peterson _et_ _al_. (_A13_), who state that the postmanufacture liberation of formaldehyde diminishes with either an increase in pressing time, or an increase in pressing temperature.

A29. Walker, J. F.
1964. Formaldehyde. 3d ed., Am. Chem, Soc.
Monogr. Ser, No. 159. Reinhold Publishing Co., Stamford, Conn.

Production, monomeric formaldehyde, aqueous formaldehyde, distillation, polymers, chemical properties, reactions with inorganic reagents, reactions with 15 types of organic compounds, quantitative analysis, uses of formaldehyde.

Comment: This edition was reprinted in 1975 by Robt. E. Krieger Publishing Co., Huntington, N.Y.

Section B. Analytical Methods

Ba. Snyder, A. D., F, N. Hodgson, M. A. Kemmer, and J. R. McKendree
1976. Utility of solid sorbents for sampling organic emissions from stationary sources. MRC-DA-567, EPA/600/2-76/201. Monsanto Research Corp., Dayton, Ohio.

The solid sorbents, porous polymers, were tested at two industrial sites as the means for sampling and concentrating trace organic compounds. A detailed discussion is given of the problems therein.

Comment: Other solids (e.g., activated carbon or charcoal, silica gel) have been used in similar fashion (B2, B3, B14, B21); the above report is concerned only with the use of porous polymers. See also B16, B29.

Bb. Bitterli, W., and J. M. Sire
1976. Detection of trace amounts of formaldehyde in aqueous solutions--comparison of two spectral colorimetric methods for the quantitative determination of formaldehyde in textiles. Textilveredlung 11(8):345-348. Chem Abs. 85:144533.

The reaction of formaldehyde with 3-methyl-2-benzothiazolone hydrazone is more sensitive than the spectrophotometric method using acetylacetone (B10, B24). See also B8.

Bc. Krikunov, N. I., T. V. Kozhukhova, E. K. Bovkun, and M. I. Bukovskii
1976. Modified method of determining formaldehyde in the air using phenyl-hydrazine. Metody Anal. Kontrolya Proizvod. Khim. Promsti. 2(1976):32-33. Chem. Abs. 85:98632.

Formaldehyde reacts with sodium sulfite-stabilized phenylhydrazine and HC1 in the presence of an oxidizing agent. The stabilized reagent remains unchanged for 10 days. The color intensity is measured optically or visually. The sensitivity is 1 microgram in 4 milliliters of solution.

B1. Clermont, L. P., and M. N. Carroll
1976. Improved chromotropic acid determination of formaldehyde evolution from wood composites. For. Prod. J. 26(8):35-37. Chem. Abs. 85:162220.

The authors describe a simple procedure for determining the amount of "evaporable" formaldehyde (A23, B33) evolved from particleboard which is ground first in a Wiley mill. The amount of formaldehyde (log scale) released is a linear function of the temperature to which the sample is heated.

The limit of detection is near 0.5 mg/m^3 (0.4 ppm) or 1 microgram of formaldehyde.

Comment: The preparatory procedures (grinding and conditioning for MC) would be expected to have some effect upon the accuracy of the results. Thus, depending upon the initial MC of the sample, conditioning at 50 percent RH for 2 days may or may not enhance loss of HCHO. Grinding in a Wiley mill, unless special cooling is provided, tends to raise the temperature of the material, increasing the rate of HCHO loss as shown by the authors' data for the effect of temperature. It has been shown by others (see Section A) that the liberation of formaldehyde is enhanced by an increase in humidity and/or temperature. A similar procedure was reported by Christensen (B30).

B2. Levadie, B., and S. M. Macaskill
1976. Analysis of organic solvents taken on charcoal tube samplers by a simplified technique. Anal. Chem. 48(1):76. Chem. Abs. 84:64737.

The technique of using a charcoal tube sampler plus gas chromatograph for analysis (qualitative and quantitative) is described in its application to monitoring the workplace where paint and lacquer solvents were used. Formaldehyde was not covered in this work, but other oxygenated compounds were,

Comment: This report and others similar to it (e.g., B14, B15, B20) are inluded in this review to bring to the readers' attention the increasing importance of surveillance methods which will be required in order to comply with OSHA standards. The charcoal sampler tube–carbon disulfide desorption–gas chromatograph system has already been accepted by OSHA as a method for compliance investigations (B20). The sorbent tube method of collecting low–level atmospheric pollutants is gaining favor; the sorbent filling need not be limited to activated carbon (charcoal) as may be noted in citations following.

B3. Flick, K.
1975. Determination of formaldehyde concentration at the factory in the production of chipboards. Zentralbl. Arbeitsmed. Arbeitsschutz 25(9):257–263. Chem. Abs. 84:110749. (Ger.).

Water was used to desorb formaldehyde collected by sorption on silica gel. The aqueous solution was analyzed by the pararosaniline method (B40). In the range of 0.06- to 0.12-mg formaldehyde, the relative standard deviation was -3.3 to -6.7 percent.

Comment: It is presumed (though no description is given in the abstract) that the sample was collected by the sorbent-tube method (B2), silica gel being a dry, granular solid. The advantages of such a sampling technique will be recognized from later citations and from the fact that it can be made very simple and portable for localized, personnel workplace sampling. See also B38 and B43.

B4. Mohl, H. R.
1975. A nondestructive rapid test for determining formaldehyde liberation from particleboards without overlays. Holz-Zentralbl. 101(67):869,871. (Ger.).
A suction apparatus is used suitable for production control, investigation of complaints, and research,

Comment: Being nondestructive to the specimen material, the method obviates the limitations and criticisms of the method (B1) described earlier.

B5. Roffael, E.
1975. Measuring formaldehyde release. A practice-related method of determining the formaldehyde release of urea resin bonded particleboard construction panels. Dtsch. Holz-Ztg.(101):1403-1404 (Ger.).

Formaldehyde released from small samples of the panel under test is absorbed in water; the amount of HCHO is determined quantitatively using the iodometric method (A29, B33). The water and samples are contained in a tightly sealed bottle, which is placed in a constant temperature enclosure. The author reports data for the effect of the following parameters on the release of HCHO from particleboard: (1) molar ratio of urea to HCHO, (2) storage time, (3) press time, (4) curing agent, (5) phenol- versus urea-formaldehyde resins, (6) temperature of board in use, (7) type of raw material--i.e., wood versus bark, which had a high phenolic components content.

B6. Chrastil, J., and J. T. Wilson
1975. Sensitive colorimetric method for formaldehyde. Anal. Biochem. 63(1):202-207. Chem, Abs. 82:94959.

A colorimetric procedure which is sensitive to formaldehyde at the nanomole level (1 n mole of HCHO = .030 µg). A violet color is obtained when formaldehyde reacts with tryptophan in the presence of H_2SO_4 and Fe, Ni, or Co. The reaction is very specific. See following citation, B7.

B7. Becker, K. H., V. Schurath, and T. Tatarczyk
1975. Fluorescence determination of low formaldehyde concentrations in air by dye laser excitation. Appl. Opt. 14(2):310–313. Chem. Abs. 82:144410.

A technique for measuring formaldehyde in air (at atmospheric pressure) in the subparts per million range. The technique is capable of a considerable increase in sensitivity permitting concentrations of formaldehyde in air to be determined in the parts per billion range. The present limit is 5 ppm.

B8. Ohtomi, M., T. Ohno, and S. Akabori
1975. Determination of formaldehyde in water with 3–methyl–2–benzothiazolone hydrazone. Kogyo Yosui (202):21–24. Chem. Abs. 84:126595. (Jap.).

A colorimetric method suitable for the determination of formaldehyde at low concentrations in water. The reaction of HCHO with 3-methyl-2-benzothiazolone hydrazone, sulfamic acid, and $FeCl_3$ produced a color stable for 17 hours in the range 30 parts per billion to 1.5 ppm.

B9. Technical Association of the Pulp and Paper Industry
1976. Analysis of formaldehyde in aqueous solutions and of free formaldehyde in resins. TAPPI Official Standard T600os–76. TAPPI, Atlanta, Ga.

A standardized sodium sulfite (B33) procedure suitable for analysis of aqueous solutions of formaldehyde gas. The method has been found to be adaptable to determination of free or unreacted HCHO in urea–formaldehyde resins (B33).

B10. Kojima, S., and T. Oba
1975. Analyses of harmful chemicals in household necessities. I. Determination of free formaldehyde in underwear. Bunseki Kagaku 24(5):294-298. Chem. Abs. 83:116643. (Jap.).

Aqueous solutions of formaldehyde are analyzed photometrically by the acetylacetone method, the Hantzsch reaction (A29) between HCHO, acetylacetone, and an ammonium salt to give a yellow derivative. The quantities of HCHO in the various items of clothing ranged from 0 to over 600 ppm.

Comment: See Section D. Toxicology, in which the allergenic properties of formaldehyde appear to be of considerable importance from the standpoint of both inhalation and skin contact.

B11. Viccaro, J. P., and E. L. Ambye
1975. Determination of glycolic acid. U.S. Patent No. 3,915,638. Chem. Abs. 84:38441.

The reaction of formaldehyde with 2-naphthol in H_2SO_4 solution produces a yellow-green colored product which can be quantitated photometrically. The detection limit was 0.08 microgram HCHO.

B12. Sawicki, E., and C. R. Sawicki
1975. Aldehydes: Photometric Analysis. Volumes I and II. Academic Press Inc., New York. Chem. Abs. 84:53638.

The two volumes are concerned with aldehydes and their precursors. Many of the reactions could be useful in other fields: mass spectrometry, gas chromatography, high-pressure liquid chromatography, and others. The analytical methods are concerned only with liquid solutions, however, and hence, the wet chemistry. The volumes contain analytical data and procedures for 66 aldehydes. The authors believe that the information provided allows for development of many more characterizations and assay methods than they have provided. Formaldehyde is covered in Vol. 1, Ch. 23, p. 200-246.

B13. Gosink, T. A.
1975. GC in environmental analysis, Environ. Sci. Technol. 9(7):630-634. Chem. Abs. 83:136427.

A review of the capabilities and. applicability of the gas chromotographic technique. The versatility and extreme sensitivity of which it is capable make it a tool which has been applied to every aspect of analytical chemistry.

Comment: This citation, like the previous one, is included for guidance. The author presents a particularly clear and concise discussion of the topics; he does not gloss over shortcomings and limitations of the technique. Several applied examples are of interest, expecially with respect to trace metals analysis. These could be germane to the wood-using industries in as much as trees are capable of selectively concentrating metals depending upon soil conditions, and some metals find application as wood preservatives.

B14. Pellizzari, E. D., J. E. Bunch, B. H. Carpenter, and E. Sawicki 1975. Collection and analysis of trace organic vapor pollutants in ambient atmospheres. Technique for evaluating concentration of vapors by sorbent media. Environ. Sci. Technol. 9(6):552–555. Chem. Abs. 84:64642.

Polymer beads (B16, B29), activated carbons (B20, B21), and gas chromatographic–type packings (liquid phases coated onto solid supports) were tested with three synthetic mixtures of toxic vapors. (Formaldehyde was not one of the components.) The objective of the work was to evaluate collection efficiency from ambient atmosphere at the nanogram per cubic meter level (1 ng = 1 x 10^{-9} g = 1 x 10^{-6} mg). Most of the sorbents tested had collection efficiencies of 90 percent or better for the three test mixtures. A flame ionization detector was used as the monitoring device, Problems and precautions in using such collection systems are discussed. There is an extensive bibliography of collection and concentration methods reported in the literature.

Comment: While this paper, and the related one following, do not deal with formaldehyde as such, the techniques and principles investigated are important in view of the trend in industrial health and safety (B20, B32) embodied by the Occupational Safety and Health Act (OSHA).

B15. Pellizzari, E. D., J. E. Bunch, B. H. Carpenter, and E. Sawicki 1975. Collection and analysis of trace organic vapor pollutants in ambient atmospheres. Thermal desorption of organic vapors from sorbent media. Environ. Sci. Technol. 9(6):556–560. Chem. Abs. 84:8440.

Synthetic air pollutant mixtures, concentrated by adsorption on tubes of sorbent media, were desorbed and analyzed by gas–liquid chromatography (GLC). Because of limited sensitivity with available detectors, the objective of the work was to determine the efficiency with which the entire amount of sorbed vapors could be transferred to the analytical system.

Comment: See previous reference. In addition, the present work is applicable to analytical detection systems other than GLC, but where a sorbent–type concentrating procedure has been used to increase sensitivity.

B16. Bertsch, W., E. Anderson, and G. Holzer
1975. Trace analysis of organic volatiles in water by gas chromatography–mass spectrometry with glass capillary columns. J. Chromatogr. 112, 701–718. Chem. Abs. 84:126598,

Gas phase stripping of trace amounts of volatile organic compounds in water is used to transfer such to a porous polymer. Heat desorption from the latter sorbent is used to transfer the volatiles to a gas chromatography column for analysis. See B29 also.

B17. Energy Resources Co., Inc.
1975. A review of concentration techniques for trace chemicals in the environment. Energy Resource8 Co., Inc., Cambridge, Mass. Nov. 489 p.

The format of the report gives a general description of the numerous methods of concentrating trace chemicals from water, air, and solids (principally soil and plant material). Each section includes two types of tables: (a) by method of concentration and (b) by materials concentrated. Each is accompanied by the pertinent literature references. Formaldehyde is not one of the specific compounds covered; there is, however, a heading for aldehydes in general.

B18. Oblivin, A. N., and G. N. Afanas'ev
1975. Determination of formaldehyde and methanol evolved in the polycondensation of resins under chipboard hot forming conditions. Izv. Vyssh. Uchebn. Zaved., Lesn. Zh. 18(2):104–108. Chem. Abs. 84:18150. (Russ.).

Adhesives of the type used in making particleboard were decomposed at known temperature and pressure. The apparatus used permitted analysis, by gas chromatography, of small fractions of the volatiles formed, including formaldehyde.

B19. Harkin, John M., John R. Obst, and William F. Lehmann
1974. Visual method for measuring formaldehyde release from resin-bonded boards. For. Prod. J. 24(1) :27-30. Chem. Abs. 80:110110.

Two test procedures are described: One permits measurement of the formaldehyde released to the air from a board sample; the other is a nondestructive spot test which differentiates between boards capable of releasing formaldehyde (purple spot) and those that show little or no liberation (dull brown spot). The reagent (purpald) is sufficiently sensitive that formaldehyde concentrations below the threshold of human detection, 1.0 mg/m^3 (0.88 ppm), can be detected. Several model applications are described. One of these demonstrates how formaldehyde release varies with degree of cure, and illustrates how the spot test is applicable to routine control use or onsite testing of complaints. Accurate assay of HCHO with purpald requires that the test be carried out under standardized conditions,

Comment: The "airflow procedure" avoids the need to collect the airborne formaldehyde in any type of liquid or solid reagent. See B20 and B21.

B20. Mueller, F. X., and J. A. Miller
1974. Determination of organic vapors in industrial atmospheres.
Am. Lab, 6(5):49–50,52,54,56,58–61.
Chem. Abs. 81:140395.

No data are given for formaldehyde. Vapor concentration measurements are made by a combination of methods; four examples demonstrate application of these. Limitations are discussed.

Comment: The paper illustrates how one industrial company utilized OSHA standard methods for compliance investigations, in combination with existing laboratory instrumentation (GC), to monitor inhouse situations. Such procedures (e.g., B19) will be important to board manufacturers if the experience reported by Freeman and Grendon (B32) are indicative of the trend in safety precautions. The situation as regards formaldehyde will be spelled out more clearly when the NIOSH criteria document on formaldehyde[6] is published (see also D1).

B21. Burnett, R. D., Philip Diamond, M. P. Anderson, and M. L. Swigart
1974. Evaluation of charcoal sampling tubes. p. 34 EHL–74M–13.
USAF Environmental Health Lab, McClellan AFB, Calif. Sept.

See B2, B20, E4. Experimental tubes were compared with commercial charcoal tubes,

Comment: While charcoal tubes are a convenient means for collecting solvent vapors, there are limitations. Lee (E12) points out that the capacity of activated carbon for formaldehyde varies directly with relative humidity. Thus, variable results would be obtained if humidity changed during a sampling period. See B38.

B22. Chand, R.
1974. Apparatus and process for electrochemical gas determination. Ger. Offen. 2,354,149. Chem. Abs. 81:114221 (Ger.).

An electrochemical sensor for formaldehyde in air. (See B27 and B34.) The sensors could be used for determining other gases and vapors.

B23. Paronyan, R. V., and V. K. Sarkisyan
1974. Determination of formaldehyde by gas-liquid chromatography in a mixture of primary aldehydes, alcohols and acids. Zh. Anal, Khim. 29(3):604-606. Chem. Abs. 81:9495 (Russ.).

The procedure described allows separation of a mixture of C_1 — C_4 aldehydes, alcohols, and acids using a column packing composed of 5 percent TWEEN-60 + 2 percent azelaic acid on Polychrome-1.

Comment: See also B35. Polychrome is a fluorplast of limited thermal stability; Polysorb is recommended (B35). Unfortunately, the direct measurement by GC of hazardous compounds in air at the low ppm range (e.g., <10, the limit of Paronyan's paper) is difficult without preconcentration. And in the parts-per-billion range, it is virtually impossible without a system for concentrating trace vapors. (See B7, B14, and B20.)

B24. Honma, S., and M. Kitayama
1974. Formaldehyde contents in clothing. Hakkaidoritsu Eisei Kenkyusho Ho (24): 128-131. Chem. Abs. 83:116646. (Jap.).

Two photometric procedures are described, based on the reaction of formaldehyde with (a) acetylacetone (A29, B10, B25) and (b) phloroglucino (A29). Nylon clothing was found to contain from 0 to 1,336 ppm of HCHO.

Comment: The reactions of formaldehyde with phloroglucinol as described by Walker (A29) led to water-isoluble resins. The use, therefore, of this reagent in a photometric analysis is questionable, based at least on the small amount of information in the published abstract.

B25. Yoshihara, T., C. Okumoto, K. Terashima, and others
1974. Testing method for hausehold articles containing poisonous chemical substances. II. Determination of formaldehyde in commercial underwear for ladies and infants. Tokyo Toritsu Eisei Kenkyusho Kenkyu Nempo (25):103-110. Chem. Abs. 83:11943. (Jap.).

A water extract of a cloth sample was analyzed using the acetylacetone-formaldehyde reaction (A29, B10, B24).

B26. Kurata, D., and S. Takahashi
1974. Assay of formaldehyde gas concentration in the silkworm rearing room sprayed with formalin solution. Nippon Sanshigaku Zasshi43(3):245-249. Chem. Abs. 82:52472. (Jap.).

An aqueous solution of 2-hydrazinobenzo-thiazole was found to be a better absorbent for formaldehyde gas than water alone. See also B17.

B27. Marcote, R. V., R. Chand, and T. H. Johnston
1973. Development and evaluation of a portable aldehydes analyzer. Anal. Instrum. (11):31-43. Chem. Abs. 79:61282.

An electrochemical analyzer for direct measurement of formaldehyde at the ppm concentration level in ambient air and process gases. (See B7 and B16 for other sensitive instrumenta1 methods.)

B28. Minemura, N., and H. Takahashi
1973. Analysis of dilute formaldehyde solutions by gas chromatography. Rinsan Shikenjo Geppo (12):1–4. Chem. Abs. 80:140918 (Jap.).

This is apparently not a trace–level procedure, as aqueous solutions of formaldehyde ($\geq$10 ppm) were analyzed. The formaldehyde was reduced first to methanol for the GC analysis, thus permitting the authors to use the very sensitive flame ionization detector which is not sensitive to formaldehyde itself.

Comment: At concentrations high enough to allow the use of the thermal conductivity detector, there is little value in the conversion of formaldehyde to methanol, as formaldehyde and water can be resolved by several of the available porous polymer packings. For another approach, see Bertsch, Anderson, Holzer (Bl6).

B29. Frankel, L. S., K. L. Wallisch, and others
1972. Selective retention by porous polymer adsorbents. Application to formaldehyde determination. Anal. Chem. 44(14):2401–2402. Chem. Abs. 78:61830.

The chromatropic acid method is supplmented by the use of a tube of a porous polymer absorbent to remove pollutants which interfere with the formaldehyde determination. A sensitivity of an order lower than 3 ppm formaldehyde in air is claimed thereby. The amount of polymer used is too small to affect the quantitative measurement of formaldehyde. See reference B16.

B30. Christensen, R. L.
1972, Test for measuring formaldehyde emission from formaldehyde resin bonded particleboards and plywood. For. Prod. J. 22(4):17-20. Chem. Abs. 77:7567.

The objective was to be able to predict the extent of formaldehyde liberation from particleboard and which factors were influential. To this end, an analytical procedure was devised whereby free formaldehyde was determined by heating a sample of ground board in vacuum and (collecting the formaldehyde in ice water. The latter aqueous solution was titrated by the sodium sulfite method (A29).

Comment: The procedure may be suitably characterized as an accelerated test for total evaporable formaldehyde (see definitions in A23, B33). On the other hand, the purpald spot test (B19) is instantaneous, nondestructive, and therefore, capable of being used as a quality-control test for finished boards. For reasons stated previously (B1), this author questions the preparatory procedure of grinding and conditioning samples.

B31. Smith, R. G., R. J. Bryan, M. Feldstein, and others
1972. Tentative method of analysis for low-molecular-weight aliphatic aldehydes in the atmosphere, Health Lab. Sci. 9(1):75-78, Chem. Abs. 763103382.

A combination of methods is utilized to determine formaldehyde (chromotropic acid) , acrolein ($HgCl_2$-helcylresorcinol procedure) and C_2 — C_5aldehydes (gas chromatography), A sample of these air pollutants is collected with 1 percent sodium bisulfite solution in midget impingers.

Comment: Other procedures have been used to collect formaldehyde for analysis; for example, see B3, B26, B29, B33, B40.

B32. Freeman, H. G., and W. C. Grendon
1971. Formaldehyde detection and control in the wood industry. For. Prod. J. 21(9):54-57. Chem. Abs. 76:5043.

Their procedure for using the chromotropic acid test for formaldehyde allowed concentrations to be measured in the range 0.04 to 8.0 ppm. The procedure was adapted to checking various adhesivesfor formaldehyde evolution properties before the adhesive was used in their industrial plant. Impetus for the work was twofold: Increasing instances of accidents and indications by employees that they believed the odor of formaldehyde was a contributing cause. Experience showed that workers objected when the formaldehyde odor exceeded 1 ppm. As a result, a ceiling value of 2 ppm, rather than the usual 5 ppm, is their recommendation. (See also Sgibnev, D28, who investigated the physiological effects on man of low concentrations of formaldehyde.) Of the variables evaluated--plant temperature and humidity, glue type, product being made--only glue type was significant.

B33. Schwarz, F. E.
1971. Advances in detecting formaldehyde release. Proc. 5th Particleboard Symp. p. 31-44. Wash. State Univ., Pullman.

The author reviews the analysis for formaldehyde with respect to the chemical aspects of resin formulation and the wood-resin aspects of board production, Both areas are dependent upon good analytical procedures for formaldehyde. Topics discussed are: formaldehyde detection (nine procedures), collection, release apparatus, and release parameters. He gives recommendations for correcting and controlling the formaldehydeirelease problem. Significantly, he recognizes initially that it is a toxic chemical, and one which, because of its low levels of initial odor and discomfort detection by man, make it one of the more irritating gases for humans. It particularly affects the mucous membranes of the eyes and nose. See also Section D and B32. He recognizes the definitions of Neusser and Zentner (A23) of four types of formaldehyde: Free--titratable in resin; Releasable — released during heating; Expellable--expelledduring pressing; Evaporable--emitted following pressing.

B34. Johnston, T, H., R, V. Marcote, and R. Chand
1971. Development of a formaldehyde analyzer for motor vehicle exhaust emissions. Final rep. No. 171. Dynasciences Corp., Instr. Systems Div., Whittaker Corp., Los Angeles, Calif, Aug. (sponsored by EPA).

See B22 for the analyzer as patented, An important section of the present report is the authors' description of a reliable formaldehyde standard in the 1 ppm range. The standard source is based on the permeation tube principle.

B35. Ustinovakaya, I. A., V. M. Chirkova, L. Ya. Gavrillina, and others
1971, Analysis of some oxygen-containing substances by gas chromatography on Polysorb with a liquid phase. Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk (6):131-4. Chem. Abs. 77:121895 (Russ.).

See B23. A mixture of water, methanol, and low molecular weight aldehydes (including formaldehyde) is separated completely by gas chromatography. Column packing is 15 percent TWEEN-80 on Polysorb.

B36. Masek, Vaclav
1971. Determination of acrolein and formaldehyde in air. Gesundh.-Ing. 92(8):245-246. Chem. Abs. 75:154689 (Ger.).

Three colorimetric methods were investigated for the analysis of mixtures of acrolein and formaldehyde. The interferences by each compound upon the other in each of the methods is detailed.

Comment: Acrolein would not be present in formaldehyde evolved from particleboard. The paper should be of interest, however, for its informational value in respect to formaldehyde analysis by colorimetric methods.

B37. Nelson, G. O.
1971. Controlled test atmospheres--principles and techniques. Am. Arbor. Sci. Publ. Ann Arbor, Mich. 256 p. Chem. Abs. 75:40062.

Provides both theoretical and practical guidance in preparing standard gas mixtures. Contents are:
(1) Introduction and general principles
(2) Air purification
(3) Flow rate and volume measurements
(4) Static systems for producing gas mixtures
(5) Dynamic systems for producing gas mixtures
(6) Specilized systems.
Because of the requirements of instrumental methods for calibration gases, the book should be of particular use to analysts employing such methods.

B38. Kachmar, E. G., and V. A. Khrustaleva
1969. Use of hard granulated adsorbents for the taking of atmospheric samples. Gig, Sanit. 34(9):87-90. Chem. Abs. 713116273 (Russ.).

The authors recommend the use of silica gel as an adsorbent for acrolein and formaldehyde in taking atmospheric samples. See also B14, B15, B20, B21, B29. See B43 for a similar application of silica gel. as the basis for a visual colorimetric indicator of concentration.

B39. Matsumoto, Tsuneo
1968. Free formaldehyde determination in urea resin adhesives by the amonium chloride method. Bull. Govt. For. Expt. Sta. (Tokyo)(212):179-185(March) (Jap.). Chem. Abs. 69:97373.

A recording autotitrator is used to determine free formaldehyde, thus eliminating the error due to the visual bromothymol blue end point.

B40. Lahmann, E., and K. Jander
1968. Formaldehyde determination in urban atmosphere, Gesundh.-Ing. 89(1):18-21. Chem. Abs. 68:89696. (Ger.).

A spectrophotometric method based on the color developed by HCHO in solution with sodium tetrachloromercurate, sodium sulfite, pararosaniline, and HCl. With a 1-hour sampling period, 2 $\mu g/m^3$ of HCHO can be detected. The authors report also that the absorption of HCHO in distilled H_2O is ≥ 98 percent efficient at a flow rate of 150 liters/hour in the concentration range of 2 to 50 $\mu g/m^3$.

B41. Plath, L.
1966. Determination of formaldehyde liberation from particle boards by microdiffusion. Holz Roh- Werkst. 24(7):312-318. Chem. Abs. 70:48817 (Ger.). Chem. Abs. 65:18830 (Ger.).

A micromethod in which diffusion of formaldehyde from a board sample is measured semiquantitatively by the chromotropic acid color reaction. The technique was used to determine that the liberation of formaldehyde was greater from the middle layer of the board (even though there was less resin in that layer) than from the surface layer. Because of the small size of sample used, representative sampling could bias the results.

B42. Monsanto Corp.
1964–65. Determination of formaldehyde evolution rate from cured amino–plast resin(s): 13O--films; 135--in wood particle products. Lab. Test Method 130, 135. Monsanto Corp., Eugene, Oreg.

An accelerated method for measuring the evolution rate from loose or consolidated wood particles and, primarily, urea–formaldehyde and melamine–formaldehyde resins. The evolved formaldehyde is absorbed in an aqueous solution of hydroxylamine HCl, and then back titrated.

B43. Hughes, E. E., and S. H. Lias
1960. Detection and estimation of low concentrations of aldehyde in air . Anal. Chem. 32(5) : 707-708. Chem. Abs. 54:14516.

Aldehyde Is absorbed from the air by silica gel (<u>B3</u>, <u>B38</u>) contained in a glass tube. A developing solution is added to the tube, and the resulting color compared with standards. Formaldehyde in air at a concentration of 10^{-8} mole percent (the stated lower limit for the method) is equivalent to 1.3 mg/m^3 or approximately 1 ppm.

Comment: Indicator tubes, based on the same principle, are available now commercially.

Section C. Control and Removal of Formaldehyde

Items are classified by the type of control method each represents: Adhesive; Adsorbent; Coating; or Ventilation.

C1. Minoji, A., T. Koma, and O. Onoura
1976. Formaldehyde odor-free coating compositions. Jpn, Kokai 76 20,225, Feb. 18, 1976, 7 p. Chem. Abs. 85:7355.

Coating: A varnish was prepared such that the coating itself was free of formaldehyde odor by virtue of containing an acid amide polymer which acted as a scavenger for HCHO. The content of scavenging polymer was variable.

Comment: A coating as described should be particularly effective for various wood-base fiber and particle-panel materials found to be evolving formaldehyde after installation. Not only would the board surface (and edges also) be sealed against exposure to atmospheric humidity, but the emission of HCHO to the air would be reduced twofold by the scavenging action of the polymer and reduced diffusion through the varnish coating. As seen from Section A, humidity is an important parameter in the rate of formaldehyde release from such wood-panel products bonded with formaldehyde-based adhesives.

C2. Roffael, E., W. Rauch, and C. Von Bismarck
1975. Formaldehyde liberation and strength development during the gluing of oak chips with urea-formaldehyde resins, Holz Roh-Werkst, 33(7):271-275. Chem. Abs. 83:207198. (Ger.).

Adhesive: Addition of a hardener, NH_4C1 + NH_4OH + urea, to urea-formaldehyde resin adhesive resulted in a substantial decrease in the liberation of HCHO from particleboards made from pine and oak. In the case of the oak board, the mechanical properties were affected negatively. Omitting NH_4Cl from the hardener overcame this deficiency without negating the other advantage. The hardener reduced HCHO emission during both pressing and storage.

Comment: Both urea and ammonium salts have been used in various other ways to reduce formaldehyde odor. (See, e.g., C4, C5, C8, C9, C11).

C3. Minemura, XI, S. Imura, S. Hirata, and others.
1975. Effects of reinforcing materials on properties of glue and plywood. Rinsan Shikenjo Geppo 1975 (284):5-9. Chem. Abs. 84:123688. (Jap.).

Adhesive: The emission of formaldehyde from plywood was reduced by the addition of melamine or potato protein + urea to the adhesive formula; the moisture content of the veneer used should also be low. See also A2.

C4. (a) Minemura, N., S. Hirata, and H. Takahashi
1975. Effects of chemicals on free formaldehyde emission from treated plywood. Rinsan Shikenjo Geppo (1):13-16. Chem. Abs. 83:30193. (Jap.).

(b) Sasaki, T.
1974. Formalin odor free plywoods. Jpn. Kokai 74 125,504. Dec. 2, 1974. Chem. Abs. 83:12652. (Jap.).

Coating: Plywood was immersed in aqueous solutions of various ammonium salts, e.g., ammonium thiosulfate and -sulfite (C4a), or -acetate (C4b), and then dried. The evolution of HCHO decreased as pH increased of the mixtures (C4a).

Comnent: This appears to be a drastic, if not unnecessary, procedure. Similar results have been achieved by (spray) coating wood-board products with ammonium salt solutions (C9) or other nitrogen-containing compounds such as urea (C5, Cll) or other amides (C14).

C5. (a) Suematsu, A., and H. Yamada
1975. Odorless plywood, Jpn. Kokai 75 24,404, March 15, 1975. 5 p. Chem. Abs. 83:99536.

(b) Kunii, Y., and Nishiyama, Y.
1975. Plywood. Jpn. Kokai 75 24,413, March 15, 1975. 5 p. Chem. Abs. 83:99537.

(c) Kitakado, Y.
1974. Odorless plywood. Jpn. Kokai 74 66,808, June 28, 1974. 5 p. Chem. Abs. 82:5530. (Jap.).

(d) Kitakado, Y.
1973. Formaldehyde odor-free plywood. Jpn. Kokai 73 72,308, Sep. 29, 1973. 5 p. Chem. Abs. 80:49540.

Coating: In plywood manufacture, before pressing, the several inner and/or outer veneers were precoated with an aqueous solution of urea in each of these four citations.

Comment: The use of N-containing (amino) compounds, urea in particular, is widespread both in the fashion described here, and as a coating applied only to the face surfaces of finished plywood (C11) in various ways, The amino compounds act as scavengers for free formaldehyde (C1).

C6. Dashkovskaya, Z. F., T. G. Zakharov, T. L. Kravchenko, and others 1975, Diminishing the evolution of formaldehyde from products containing wood particles and carbamide resins. U.S.S.R. 480,555, Aug. 15, 1975. Chem. Abs. 83:166118. (Russ).

Adhesive: Mineral oil (spindle oil) containing sodium silicate was added to reduce the evolution of HCHO from a particleboard product,

C7. Labzova, L. V., N. V. Parmonova, G. Andreeva, and others 1975. Purification of gaseous emissions during manufacture of chipboard. Plast. Massy (5):23-24. Chem. Abs. 83:136443. (Russ.),

Adsorbent: Waste gases containing NH_3 and HCHO produced during the hot pressing of chipboard were passed through catalyst beds at 400° C. Total oxidation of formaldehyde and decomposition of ammonia took place on the two most effective catalysts: A1-Pt and Pd. Each catalyst was still active after 400 hours operation. See also C18, C19, C30.

C8. Kawahara, N., and K. Takashima 1975. Removal of free formaldehyde from particleboards, Jpn. Kokai 75 43,181, April 19, 1975, 4 p. Chem. Abs. 83:99549. (Jap.).

Coating: The mat of wood chips was sprayed with aqueous urea solution prior to pressing. The concentration of formaldehyde in the air around the press was reduced by approximately threefold.

Comment: See C5 and C11 for similar processes.

C9. Ohno, K., and R. Furudera 1974. Deodorizing formaldehyde odor from resin-treated lumber. Jpn. Kokai 74 43,126, Nov. 19, 1974, 2 p. Chem. Abs. 82:141844.

Coating: Four aqueous ammonium salt solutions are described as suitable for removing formaldehyde odor from plywood. They were: (1) $NH_4C1 + NaHCO_3$; (2) NH_40Ac +. NaOH; (3) $(NH_4)_2 CO_3 + Ca(OH)_2$; (4) $NH_4C1 + Na_2SO_3$.

Comment: There is no reason, as subsequent citations will show, why any one of these should not be equally suitable for particleboard.

C10. Shirai, K., and H. Okamura
1974. Adsorbent for gaseous pollutants. Jpn. Kokai 74 109,277, Oct. 17, 1974, 4 p. Chem. Abs. 82:174861. (Jap.).

Adsorbent: A 1:1 mixture of inorganic porous materials (activated carbon was used here, however), plus powdered leather was used to adsorb formaldehyde from aqueous solution in a desiccator experiment.

Comment: Which of the two solids is really the most effective constituent is debatable perhaps. Lee (E12) points out that the capacity of activated carbon varies directly with the relative humidity. On the other hand, formaldehyde reacts actively with proteins to cause hardening and tanning as in the leather industry. Numerous other references will be cited in which protein-containing materials are utilized for their apparent scavenging action for formaldehyde.

C11. (a) Kawahara, N., and K. Takashima
1974. Plywood manufacture. Jpn. Kokai 74 108,211, Oct. 15, 1974, 4 pp. Chem. Abs. 82:172907, Chem. Abs. 82:172907. (Jap.).

(b) Hojo, Z.
1974. Removal of formaldehyde odor from plywood. Jpn. Kokai 74 75,709, July 22, 1974, 2 p. Chem. Abs. 82:32704. (Jap.).

(c) Kitakado, Y.
1973. Formaldehyde-odorless plywood, Jpn. Kokai 73 58,109, August 15, 1973, 4 p. Chem. Abs. 80:4563. (Jap.).

Coating: In plywood manufacture, both sides were spray-treated with aqueous urea solutions before and after hot pressing to give a product with reduced free formaldehyde content.

Coment: There are numerous references to the use of urea in similar fashion when a urea-formaldehyde-type resin is used in the adhesive. In some cases, the several veneer layers are each presprayed before application of adhesive and pressing (C5).

C12. Tashiro, F., T. Tanno, and T. Sando
1974. Phenolic resin-neoprene rubber blend adhesives free of formaldehyde odor. Jpn. Kokai 74 101,418, Sep. 25, 1974, 4 p. Chem. Abs. 82:141030, (Jap.).

Adhesive: Thermosetting phenolic resins, variously modified, were blended with neoprene rubber to give adhesives free of formaldehyde odor. Sail cloth was bonded to stainless steel with the resulting adhesive.

C13. Kitakado, Y.
1974. Odorless plywoods. Jpn. Kokai 74 80,210, Aug. 2, 1974, 5 p. Chem. Abs. 82:45525. (Jap.).

Adhesive: An organic amino compound (urea in this case) was added to a urea-formaldehyde resin and acid treated to pH ≤ 6. Flour (unspecified) and soybean flour were also constituents of the adhesive,

Comment: While various flours, with or without adhesive properties, are added as fillers and/or extenders, they may function also as scavengers for formaldehyde due to their protein content. See also C3, C10, C15.

C14. Kobayashi, K.
1974. Mildew-resistant decorative plywood boards with low levels of formaldehyde odor, Jpn. Kokai 74 71,103, July 10, 1974, 4 p. Chem. Abs. 82:45451. (Jap.).

Coating: Plywood, laminated with thin decorative paper, was coated on the other side with a 30 percent aqueous solution of an amide while still hot and piled up. Using the desiccator method, there was an 80-fold decrease in free formaldehyde--i.e., from 16 ppm (untreated) to 0.2 ppm (treated) in the boards.

C15. Kawashima, M.
1974. Plywood boards free of formaldehyde odor. Jpn. Kokai 74 71,118, July 10, 1974, 2 p. Chem. Abs. 82:45450. (Jap.).

Adhesive: Calcium lignosulfonate was added to urea and/or melamine resin adhesive to give a formaldehyde-free adhesive for making plywood. Wheat flour was added also (see C13). The board had <0.3 ppm HCHO (desiccator method) compared with 20 to 30 ppm for the board without the additive.

C16. Inui, K., Y. Kamitaki, and T. Iizuka
1974. Plywood with low levels of formaldehyde odor. Jpn. Kokai 74 44,060, April 25, 1974, 3 p. Chem. Abs. 81:107678. (Jap.).

Adhesive: Enzymes plus wheat flour (C13) were added to a urea-formaldehyde resin to give an adhesive with low free-HCHO content, The reduced emission of HCHO from finished plywood was attributed to the enzyme.

C17. (a) Minoji, A., T, Koma, and O. Onodera
1974. Decorative boards top coating composition. Jpn. Kokai 74 38,927, April 11, 1974, 4 p. Chem. Abs. 81:107551. (Jap.).

(b) 1974. Decorative board top coating composition. Jpn. Kokai 74 38,925, April 11, 1974, 5 p. Chem. Abs. 81:107552. (Jap.).

(c) Niwa, T., and I. Ochiai
1974. Amino-alkyd resin coating compositions with low formaldehyde liberation. Jpn. Kokai 74 25,018, March 6, 1974, 3 p. Chem. Abs. 81:79503, (Jap.).

(d) Malygina, E. F.
1974. Effect of plating and additional heat treatment on the emission of noxious substances from particleboards manufactured from urea resins. Gig. Sanit. (8):95-97. Chem. Abs. 81:153945. (Russ.).

Coating: Varnish-type top coating compositions were prepared using amino or vinyl alkyd resins to which were added various compounds (scavengers) reactive to formaldehyde, The liberation of free HCHO from plywood so coated was less than 5 ppm (C17a, C17b), or negligible (C17c). Simply coating particleboard with lacquer made it suitable for use as flooring in prefabricated houses after 3 months from date of manufacture (C17d). See also C1, C22.

C18. Kobayagawa, T., and T. Nakajima
1974. Purification of formaldehyde-containing waste gas. Jpn. Kokai 74 72,179, July 12, 1974, 3 p. Chem. Abs. 82:47377, (Jap.).

Adsorbent: Waste gas containing formaldehyde was passed, at room temperature, through a MnO_2-CuO mixed catalyst bed.

A cylinder (20) x 200 mm) containing 77 grams of catalyst in tablet form operated for 12 hours without breakthrough of HCHO from air containing 35 to 40 ppm of HCHO and flowing at 0.5 m/sec. The catalyst can be regenerated.

Comment: The catalyst described would be ideal as the filling for one of the self-contained, portable odor control units manufactured for use with activated carbon (E5). The ability to be effective at room temperature overcomes the disadvantage of high-temperature operation required for a noble metal type catalyst (C7). See also C19, C24, C28, C29.

C19. Ohe, T., and K. Ikeda
1974. Formaldehyde scavengers, Jpn. Kokai 74 05,891, Jan. 19, 1974, 3 p. Chem. Abs. 81:153947. (Jap.).

Adsorbent: Formaldehyde reactive compounds (e.g., an aqueous solution of dicyandiamide) were impregnated into porous volcanic rock. The scavenging effect was greater than that of activated carbon.

Comment: The active sorbent described could be applied in a fashion similar to that suggested for the room temperature catalyst reviewed above (C18). Similar active sorbents are the alumina-permanganate material described by Hanna and Richardson (E11), and the impregnated activated charcoal of Lee (E12). See also C28, C29.

C20. Kotani, Y., and K. Kageyama
1974. Plywood free of formaldehyde odor. Jpn. Kokai 74 35,511, April 2, 1974, 4 p. Chem. Abs. 81:107677. (Jap.).

Coating: Plywood, bonded with a urea-formaldehyde resin, was treated before or after lamination with keto derivatives, with or without a small amount of basic material, to eliminate the odor of HCHO. In the example cited, there was a 15-fold reduction in HCHO measured by the desiccator method.

C21. (a) Mikhailova, A. A., E. L. Lifshits, L. T. Ivanova, and others
1974. Improvement in the sanitary-hygienic properties of wood filled urea-formaldehyde panels. Gig. Sanit. (7):86-88. Chem. Abs. 81:140393. (Russ.).

(b) Yoshimitsu, T., Y. Kawashima, and H. Katsube
1973. Deodorizing plywood. Jpn. Kokai 73 103,705, December' 26, 1973, 3 p. Chem. Abs. 80:147139. (Jap.).

(c) Goto, T.
1973. Decorative plywoods free from formalin odor. Jpn. Kokai 73 97,976, Dec. 13. 1973, 6 p. Chem. Abs. 80:122641. (Jap.).

(d) Shvartsman, G. H., R. Z. Temkina, and M. Z. Svitkin
1972. Reduction of formaldehyde evolution from particleboards. Derevoobrab. Promst. 21(5):3-5. Chem. Abs. 77:63673. (Russ.).

Ventilation: Plywood, particleboard and wood-filled plastic panels were treated during or after manufacture with gaseous ammonia; the reduction in evolved HCHO was significant, if not complete. Thus, the plastic panels were suitable for use in houses after treatment with NH_3 (C21a); plywood was passed through a drying machine (at 80° C) into which air and NH_3 were blown (C21b); plywood, after passage through NH_3 atmasphere, was wrapped in heat-shrinkable plastic films; residual HCHO after 1-week storage was 0.08 ppm (C21c) ; particleboard was treated with hot air and with NH_3 (C21d).

Comment: Neusser and Zentner (A23) pointed out that "fumigation" with ammonia gas was used in Nomay and Austria to eliminate formaldehyde odor liberated from particleboard used in house construction. As a ventilation procedure, the treatment appears to be very effective in solving onsite problems.

C22. (a) Miwa, T., and H. Tomokawa
1974. Prevention of formaldehyde odor from aminoplast-coated wood substrates. Jpn. Kakai 74 42,737, April 22, 1974, 4 p. Chem. Abs. 81:137716. (Jap.).

(b) 1974. Prevention of formaldehyde odor from aminoplast-coated wood Substrates. Jpn. Kokai 74 42,736, April 22, 1974, 4 p. Chem. Abs. 81:137717. (Jap.).

(c) 1974. Prevention of formaldehyde odor from aminoplast-coated wood substrates. Jpn. Kokai 74 42,735, April 22, 1974, 4 p. Chem. Abs. 81:137718.

Coating: A series of coating materials was formulated using an amino alkyd resin as the base plus various additives (which act as scavengers for formaldehyde) so that the coating itself released little HCHO during application. Specific additives were urea or thio-urea (C22a), ethyl carbamate (C22b), and acetamide or formamide (C22c). A curing agent was included in the three. Application of the coatings to birchwood (C22a, C22b) board resulted in a 12- to 16-fold reduction in the amount of HCHO liberated from board so treated. See also C1 and C17.

C23. (a) Miwa, T.
1974. Removal of formaldehyde from plywood. Jpn. Kokai 74 66,804, June 28, 1974, 3 p. Chem. Abs. 82:32698. (Jap.).

(b) 1974. Removal of free formaldehyde from plywood. Jpn. Kokai 74 66,806, June 28, 1974, 3 p. Chem. Abs. 82:32699. (Jap.).

Coating: Plywood board was treated with aqueous solutions of $NaHSO_3$ (C23a) or a mixture of Na_2SO_3 with urea, thio-urea, and/or their derivatives (C23b) to remove formaldehyde. The amount of HCHO (desiccator method) was reduced, respectively, by factors of 150 and 60 for the two coatings.

Comment: The reaction of formaldehyde with $NaSO_3$ is the basis of a quantitative analysis method (A29, B33).

C24. (a) Miwa, T., and H. Tomokawa
1974. Removal of formaldehyde from plywood. Jpn. Kokai 74 124,203, Nov. 28, 1974, 3 p. Chem. Abs. 83:12585, (Jap.).

(b) 1974. Removal of formaldehyde from plywood. Jpn. Kokai 74 124,207, Nov. 28, 1974, 3 p. Chem. Abs. 82:12586. (Jap.).

Adsorbent: Papers containing compounds reactive to formaldehyde were used to wrap plywood for periods up to 10 days as a means for decreasing the free formaldehyde evolution almost 10-fold. In one case (C24a), urea was incorporated into the paper during preparation of the latter. In another (C24b), paper was impregnated with an aqueous solution of ammonium sulfamate.

Comment: Inasmuch as the paper acts only as a "support" for the active compounds, it should be possible to impregnate various other porous solids (see C18, C19, C28, C29) with the same materials, and utilize such as adsorbents in the fashion suggested in reference C18.

C25. Miwa, T., and I. Ochiai
1974. Plywood free of formaldehyde odor. Jpn. Kokai 74 25,108, March 6, 1974, 3 p. Chem. Abs. 81:78905. (Jap.).

Adhesive: Plywood prepared with urea-formaldehyde containing inorganic peroxide (H_2O_2) had no odor.

C26. Ohhara, O., and T. Maeno
1974. Formaldehyde capture agents for formaldehyde thermosetting resin adhesives. Jpn. Kokai 74 131,243, Dec. 16, 1974, 8 p. Chem. Abs. 83:44217. (Jap.).

Adhesive: A formaldehyde capture agent polymer (ammonium and/or amine) salt was added to a commercial urea resin in preparing a plywood adhesive. The reduction in formaldehyde evolved from the board was 10-fold compared with the control containing no capture agent.

C27. Tendrovskaya, V. A.
1973. Use of the mathematical planning of an experiment during sanitary-chemical studies . Gig. Sanit . (12) : 77-79 Chem. Abs. 80:112057. (Russ.) .

Ventilation: A regression equation is given for calculating the amount of formaldehyde evolved for various conditions of chipboards. Parameters included were: storage time, air temperature, ratio of air/board area, and board resin content. Experimental and calculated values differed by less than ± 12 percent.

C28. Suzuki, S., and H. Honjo
1973. Cleaning agent for air. Jpn. Kokai 73 102,078, Dec. 21, 1973, 3 p. Chem. Abs. 81:16333. (Jap.).

Adsorbent: Clay (e.g., bentonite), starch, or carboxymethyl cellulose are mixed with an aqueous solution of alkali or alkaline earth metal sulfaminate, and shaped and dried. One-hundred grams of sorbent prepared from sodium sulfaminate and bentonite adsorbed 1,000 ppm of HCHO from 60 liters air/hour for 210 hours; 72.5 percent of the sulfaminate was used. See C29 also.

C29. Yoshina, T.
1973. Adsorbent for removing formaldehyde from air. Jpn. Kokai 73 93,580, Dec. 4, 1973, 3 p. Chem. Abs. 80:99785. (Jap.).

Adsorbent: Granulated activated white clay, alumina, diatomaceous earth, porous ion-exchange resin, or activated carbon were soaked with an aqueous solution of hydrazinium (hydrazine) sulfate, or chloride, and dried. The adsorption capacity was 30 mg HCHO per gram of adsorbent (white clay + 30 pct hydrazinium sulfate) for air containing 2,000 ppm HCHO passing through 70 cm^3 of adsorbent at 42 liter/hour.

Comment: Both this and the previous adsorbent (C28) should be equally applicable in a fashion suggested previously (C18). One should note, however, that all hydrazinium salts are poisonous,[9] and may also form potentially explosive compounds with formaldehyde (A29).

C30. Eguchi, T., T. Taura, and S. Iimura
1973. Catalyst for removing carbon monoxide and formaldehyde from air. Jpn. Kokai 73 75,489, Oct. 11, 1973, 9 p. Chem. Abs. 80:40716. (Jap.).

Adsorbent: One or more of the noble metal elements Ru, Rh, Pd, and Pt were used as oxidation catalysts at room temperature (20° C) and high humidity (e.g., 80 pct RH). The carrier was a yarn, thread, or fabric, made from protein fiber, or a fiber impregnated with proteins. A protein fiber containing 1 percent Pd removed 10 ppm of HCHO from air. In the form used, the catalyst has low pressure drop.

Comment: See also C18. Inasmuch as proteins themselves have high affinity (A29) for HCHO (scavenging action), their use, as here, would appear to be that of effectively increasing the "surface area" available for sorption of HCHO. The efficiency of the catalyst element is thereby greatly increased, permitting removal of HCHO at relatively low concentrations. A catalyst form such as this would be particularly amenable to design as a compact, portable recycle ventilation unit for use in removing HCHO odor from occupied spaces.

C31. (a) Ginzel, W.
1973. Hydrolysis in urea-resin-bonded particleboard. Holz Roh-Werkst. 31(1):18-24. Chem. Abs. 78:112931. (Ger.).

(b) Roffael, E.
1973. Reducing the amount of formaldehyde given off by particleboards. Holz-Zentralbl. 99(57):845-847. (Ger.).

(c) Kubitzky, C.
1973. Adhesive admixtures, Ger. Offen. 2,206,696, 20 p. Chem. Abs. 80:37848. (Ger.).

(d) Sakarada, S., Y. Miyazaki, and T. Nakai
1973. Adhesives, Jpn. Kokai 73 51,032, July 18, 1973. 4 p. Chem. Abs. 80:37828. (Jap.).

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[9] The Merck Index of Chemicals and Drugs. 1960. 7th ed. Merck and Company, Inc., Rahway, N.J.

(e) Kawahara, N., and K. Takashima
1973. Odorless plywood. Jpn. Kokai 73 72,309, Sep. 29, 1973, 4 p, Chem. Abs. 80:61329. (Jap.).

Adhesive: Significant reduction in the release of formaldehyde from plywood and particle panel materials has been obtained during manufacture by adding various materials to the adhesive binder. These additives are usually reactive to HCHO and act, therefore, as scavengers. Thus, Ginzel (<u>C31a</u>) added ammonia and urea; Roffael (<u>C31b</u>) included a phenolic resin or a phenolic resin plus sulfite liquor; Kubitzky (<u>C31c</u>) added a variety of compounds, though the principal. ones were an aliphatic amide, thio-amide, imine, or amine, One or more of these, plus hide glue and several other N-containing substances were used to prepare a stock solution, a portion of which was then added to the adhesive resin; Sakarada (<u>C31d</u>) treated the resin-flour (filler) paste with NH_4OH, ammonium carbonate, sodium sulfite and hardener; and Kawahara (<u>C31e</u>) added urea and flour (filler).

C32. Nishino, S., and H. Shikata
1972. Deodorant for formaldehyde of resin products. Jpn. Kokai 73 92,541, Nov. 30, 1973, 3 p. Chem. Abs. 80:146717. (Jap.).

Coating: The amount of formaldehyde released from building board was reduced 90 percent by spraying with an aqueous solution of a guanidine derivative (aminoguanidine-HCl).

C33. (a) Teodorescu, L., and E. Petre
1970. Release of formaldehyde during the condensation of urea-formaldehyde resins used in wood glueing. I. Factors which affect the release of formaldehyde. Ind. Lemnului 21(1): 22-27. Chem. Abs. 73:26774. (Rom.).

(b) 1970. Release of formaldehyde during condensation of urea-formaldehyde resins used in wood glueing, Ind. Lemnului 21(2):55-58. Chem. Abs. 73:77980. (Rom.).

Adhesive: The effect of both harder and additives were investigated. In the case of the former, HC caused the release of more HCHO than NH_4Cl; urea had no effect.

Sodium metabisulfite as an additive was effective, but the resulting adhesive bond was not water resistant. This fault was obviated by adding resorcinol or vegetable tanning agents as well.

C34. Braswell, J. R., D, R. Spiner, and R. K. Hoffman 1970. Adsorption of formaldehyde by various surfaces during gaseous decontamination. Appl. Microbial. 20(5):765–769. Chem. Abs. 74:20729.

Ventilation: The adsorption of formaldehyde on various surfaces was shown to be a function of atmospheric RH, a peak in the amount adsorbed occurring at 83 percent RH. Formaldehyde was more strongly adsorbed at all RH's by cotton cloth than be either glass or stainless steel.

Comment: These data point to the need for low RH and high temperature if HCHO is to be removed readily by ventilation methods of the type cited earlier. See also E5, E9.

Section D. Toxicology of Formaldehyde

Da. Kitchens, J, F., R. E. Casner, G. S. Edwards, W. E. Harward, III, and B. J. Macri.
1976. Investigations of selected potential environmental contaminants: Formaldehyde. EPA/560/2-76/009. Atlantic Richfield Corp., Alexandria, Va. Aug. 217 p.

A broad review of formaldehyde as an air pollutant, with discussion of sources (automobile exhaust emissions, specifically), analysis, toxicity, and metabolism. According to existing data, it is not mutagenic or carcinogenic in mammals, but is mutagenic for lower animals (bacteria, e.g.). It is an allergen (D14, D18, D25) and is highly toxic at low concentrations (D28), causing eye and lung damage, and affecting the central nervous system (D12, D23, D24).

Comment: As will be seen from subsequent references, there is no concensus as to whether formaldehyde is mutagenic or carcinogenic in the human. The NIOSH criteria document[6] also is notably lacking in guideline information.

Db. Patterson, R. M., M. I. Bornstein, and E. Garshick
1976. Assessment of formaldehyde as a potential air pollution problem. Vol. VIII. GCA-TR-75-32-G(8).GCA Technology Division, GCA Corp., Bedford, Mass. 29 p.

A broad review, but less comprehensive than the previous report. The authors state, however, that aerosols have a synergistic effect on human response to formaldehyde. Table 2 in the report gives the acute sensory response of man to formaldehyde vapors. Thus, exposure results in:

eye irritation threshold	0.01 ppm	5 minutes
odor threshold	0.05	"
throat irritation	0.5	"
detectable by nearly all people	1.0	"
intolerable to most people	4.0-5.0	10-30 minutes

Comment: The sorption of HCHO onto particulate matter (aerosols, dusts) increases its hazard potential, as pointed out in D16.

D1. Health Effects Research Laboratory
1976. Scientific and technical data base for criteria and hazardous pollutants--1975ERC/RTP review, EPA/600/1-76/023. U.S. Dept. HEW, Environmental Protection Agency. Health Effects Res. Lab., Res. Triangle Park, N.C. May. 464 p.

The first in a series of annual reviews of the research results of the Environmental Research Center. While formaldehyde is not covered in this report, an evaluation is given of, among others, hydrocarbons and suspended particulates (see D16). The effect of these pollutants on health, vegetation, climate, visibility, and materials is assessed; and information on analysis and control is included.

D2. Van Atta, F. A.
1976, Developing occupational health standards. Chem. Technol. 6(1): 28-29.

A brief review of how OSHA sets up standards and the relationship between NIOSH and OSHA.

D3. Christensen, H. E., E. J. Fairchild, B. S. Carroll, and R. J. Lewis, Sr.
1976. Registry of toxic effects of chemical substances. U.S. Dept. HEW, Public Health Service, Center for Disease Control, NIOSH, Rockville, Md.

In this latest edition (formerly titled: "Toxic Substances List"), the threshold level value (time-weighted average) for formaldehyde exposure is still 3 ppm (D22) with a ceiling concentration of 5 ppm, A peak concentration of 10 ppm for 30 minutes is permitted in an 8-hour work period.

D4. National Academy of Sciences
1975. Principles for evaluating chemicals in the environment. National Academy of Sciences, Wash., D.C. 454 p.

A comprehensive review and evaluation of the state of the art and science of safety assessments. The report is directed to both government agencies and industries. There are six major parts:
(1) Introduction
(2) General considerations
(3) Human health effects
(4) Nonhuman biological effects
(5) Inanimate systems
(6) Analysis and monitoring
Seven appendices give supplementary material to selected chapters. The importance accorded Part 3, "Human health effects," is shown by greater amount of space given to this topic. In general, the report deals with chemicals on a compound-type basis except for some of the major ones--mercury and lead, for example. Aldehydes (D26) are noted as a group of substances (Ch 10: "Environmental chemicals as potential

hazards to reproduction--known and possible mutagens." p. 163) capable of chemically interacting with DNA (D8, D21). (See also D6, D7.) The "Effects on behavior" (Ch 11, Part 3) of formaldehyde on human performance were observed by Freeman and Grendon (B32).

D5. National Research Council
1975. Vapor-phase organic pollutants--volatile hydrocarbons and oxidation products. Natl. Res. Counc., Wash., D.C. Oct. 672 p.

A comprehensive and critical report on vapor-phase substances which may become of concern to health and well-being. Virtually all aspects pertinent to a pollutant are covered as outlined in reference D4. Special attention is given to oxidized compounds, formaldehyde, ozone, and benzene. Because of its high water solubility, HCHO is readily absorbed in the (upper) respiratory tract tissue. And because of the large amount of exposure of latter tissues to any vapor phase pollutants, the effects of exposure to formaldehyde are rapidly apparent. The toxicologic, pathophysiologic, and epidemiologic information for HCHO are well covered and documented with literature references.

D6. Cowan, W. D., J. Hoggan, and J. E. Smith
1975. Introduction of respiratory-deficient mutants in brewery yeast, Tech. Q., Master Brew. Assoc. Am. 12(1):15-22. Chem. Abs. 83:41456.

Formaldehyde acted as a mutagen, producing strains which had characteristics different than the parent strain of yeast.

D7. (a) Sanotskii, I. V., V. N. Fomenko, G. A. Sheveleva, and others
1976. Study on the effect of pregnancy on the sensitivity of animals to chemical agents, Gig. Tr. Prof. Zabol. (1):25-28. Chem. Abs. 84:100452. (Russ.).

(b) Shumilina, A. V.
1975. Menstrual and child-bearing functions of female workers occupationally exposed to the effects of formaldehyde. Gig. Tr. Prof, Zabol (12):18-21. Chem. Abs. 84:140163, (Russ.).

Women (D7b) who were exposed to concentrations of formaldehyde in the atmosphere of work areas producing urea-formaldehyde resins suffered menstrual and pregnancy disorders. The frequency of the disorders was approximately 2.5 times as often as for controls. See also D4. Animal studies (D7a), on the other hand, showed the functional state of pregnant rats to be less affected by HCHO than nonpregnant ones.

D8. (a) Vologodskii, A., and M. D. Frank-Kamenetskii
1975. Theoretical study of DNA unwinding under the action of formaldehyde. J. Theor. Biol. 55(1):153-166. Chem. Abs. 84:39840.

(b) Traganos, F., Z. Darzynkiewiez, T. Sharpless, and others
1975. Denaturation of deoxyribonucleic acid _in situ_ effect of formaldehyde. J. Histochem. Cytochem. 23(6):431-438. Chem. Abs. 83:55522.

Theoretical studies (_D8a_) permitted calculation of denaturation (i.e., modification of protein) maps for DNA due to the action of formaldehyde. Denaturation (_D8b_) of DNA (thermal or by acid) was markedly influenced by HCHO, two mechanisms being distinguished.

D9. Kulle, T. J., and G. P. Cooper
1975. Effects of formaldehyde and ozone on the trigeminal nasal sensory system, Arch. Environ. Health 30(5):237-243. Chem. Abs. 83:1783.

Animal studies showed that exposure to formaldehyde vapor resulted in a decrease in nasal sensory response which varied directly with the HCHO concentration. Exposure to pure air for an equal period of time resulted in only partial recovery of nasal sensitivity. See also _D24_.

Comment: These results confirm human response to formaldehyde--namely, that some workers develop a physical tolerance to repeated exposure of low concentrations of HCHO (_D10_).

D10. U.S. Department of Health, Education and Welfare, National Institute for Occupational Safety and Health.
1975. Working with formaldehyde. U.S. Dept. HEW, Public Health Service. Center for Disease Control, NIOSH, Rockville, Md.

A brochure prepared for public distribution. While no quantitative data are given, the language used is strongly cautionary. Toxicological effects of formaldehyde are discussed with respect to inhalation of the gas, ingestion of an aqueous solution, skin contact, and reactions by individuals who have an allergic sensitivity. See also _D4_, _D12a_, _D12b_.

D11. (a) U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health
1975. Part II. Toxic substances list. Fed. Regist. _40_ (121, June 23):26445-26446.

(b) Sax, N. I.
1975. Dangerous properties of industrial materials. p. 775–776. 4th ed. Van Nostrand Reinhold, New York.

A list (D11a) of chemical compounds, developed as a subset from the "Toxic Substances List" (D3), which have been reported in the literature to have produced an observed or suspected carcinogenic response in animals. This list includes agents causing both benign and malignant tumors. No data are given, nor literature references. Formaldehyde is included in this list of "Suspected Carcinogens." (See also D21.) This latest edition of of the standard reference text (D11b) now carries the precaution, under "Toxicity" of formaldehyde, "a suspected carcinogen of the lung."

D12. (a) Kuzmenki, N. M., A. I. Buslenki, S. E. Kataeva, and others
1975. Sensitizing effect of formaldehyde during production of plastics. Vrach. Delo (6):131–134. Chem. Abs. 84:21636. (Russ.).

(b) Ostapovich, I. K.
1975. Features of the sensitizing action of sulfur dioxide and formaldehyde in various regimens of their inhalation. Gig. Sanit. (2) 9–13. Chem. Abs. 83:1659. (Russ.).

(c) Basmadzhieva, K., T. Burkova, M. Argirova, and others
1974. Biological effect of threshold concentrations of hydrochloric acid and formaldehyde inhaled into the organism. Khig. Zdraveopaz. 17 (5) : 480–486. Chem. Abs. 83:72901. (Bulg.).

(d) Kolesnikov, P. A.
1974. Action of formaldehyde on the course and outcome of acute radiation sickness. Radiobiologiya 14(5):778–781. Chem. Abs. 82:81352. (Russ.).

(e) Vinogradov, G. I., I. A. Chernichenko, and E. M. Makarenko
1974. Allergenic activity of motor traffic exhaust gas. Gig. Sanit. (8):l0–13. Chem. Abs. 82:76649. (Russ.).

(f) Volkova, Z. A., and E. A. Sidorova
1971. Formaldehyde content in the blood of persons working in contact with urea–formaldehyde resins. Gig. Tr. Prof. Zabol. 15(5) :44–46. Chem. Abs. 75:101000. (Russ.).

(e) Kratochvil, I.
1971. Health hazards caused by formaldehyde liberated from anticrease textile finish. Prac. Lek. 23(10):374–375. Chem. Abs. 77:57285. (Czech.).

(h) Trinkler, H.
1968. Working with formaldehyde. Med. Lab. 21(12):283–290. Chem. Abs. 70:104703. (Ger.).

In addition to the toxic health effects noted earlier, other changes in the normal, healthy functioning of body organs and systems have been reported. In the production of plastics (<u>D12a</u>), the release of formaldehyde even at concentrations below the permissible maximum (0.5 mg/m^3) caused overt and latent sensitization of skin, lungs, stomach, and intestines. Animal studies showed that (<u>D12b</u>) at 2 to 15 mg/m^3 there were changes in the blood and in the neural response of muscle tissue; at 2 to 7 mg/m^3 there was also a sensitizing action. Inhalation (rats) of HCHO at 0.35 mg/m^3 for 3 hours per day for 6 months resulted in tissue changes in the liver, indicating faulty nutrition (<u>D12c</u>). The normal functioning of both the liver and blood system of mice was altered by the inhalation of formaldehyde (<u>D12d</u>). And guinea pigs, which 'inhaled HCHO at a level of 0.011 to .38 mg/m^3 for 8 hours per day during 3 weeks, also exhibited damaged blood system function (<u>D12e</u>). Workers and sales persons exposed to urea–formaldehyde resin were found to have formaldehyde in their blood at various concentrations; the HCHO reached the blood stream by inhalation or through the skin (<u>D12f</u>). Personnel exposed to formaldehyde vapor as a result of ironing new clothes (treated for anticrease properties with a urea–HCHO resin) suffered from inflammation of the eyelids and the nose and throat membranes, and exhibited long–term bronchitis (<u>D12g</u>). Individuals using formaldehyde (presumably a formalin solution) as an histological fixative exhibited eczema and inflammation of the bronchial tract (<u>D12h</u>).

D13. Weiss, I. J.
1974. A new reference approach to chemicals found in consumer products. Consum. Prod. Saf. Comm., Bur. Biomed. Sci. Wash., D.C, Dec. 81 p.

Describes a project designed to provide information about selected chemicals used in consumer products of interest to CPSC. Complete information on ingredients in a product is required (by CPSC)––e.g.,chemical structure, methodology, toxicity, carcinogenicity, mutagenicity, and teratogenicity.

Comment: It will be recognized that a home building material, such as particleboard made with a urea–formaldehyde type adhesive, and which evolves formaldehyde, could be subject to control by CPSC. Furthermore, because the HCHO would constitute an environmental air pollutant (in the home, for instance), EPA would be concerned; and, at the point of manufacture, where an occupational hazard could exist, OSHA rules would prevail. See also D1–D5, D10, D11a.

D14. Schorr, W. F., E. Keran, and E. Plotka
1974. Formaldehyde allergy. Arch, Dermatol. 110(1):73–76.
Chem. Abs. 82:26691.

Quantitative analysis of 112 samples of women's fabric samples showed none to be completely free of formaldehyde; the range was from 1 to over 3,500 ppm. The authors have seen (in clinical practice) patients with extreme HCHO allergy and corresponding intractable clothing dermatitis.

Comment: The chemical nature of HCHO is such that it is strongly sorbed by many materials, and highly soluble in water. Thus, clothing exposed to airborne HCHO vapor would become contaminated, the level of which would increase with increasing RH as water also is a strongly sorbed substance. The net result would be to increase the possible level of irritation to skin of a sensitive individual. Primary irritation of the eyes, upper respiratory tract and skin is one of the most characteristic effects of aldehydes, especially of the lowest molecular weight ones; formaldehyde is the most critical in these respects (D5, p. 275). Newer data indicate some possible absorption of vapors by skin, with more water soluble substances such as HCHO likely to penetrate (D5, p. 269).

D15. Takhirov, M. T.
1974. Combined action of six air pollutants on the human body.
Gig. Sanit. (5):lOO–102. Chem. Abs. 81:110854. (Russ.).

Six air pollutants (acetic acid, acetic anhydride, acetone, formaldehyde, phenol, and hydrochloric acid) were additive in their effect on the nose and in their electroencephalographic action if the amounts were expressed as fractions of the threshold values.

D16. Conte, C., and G. Devitofrancesco
1973. Choice of parameters for the estimation of hazard industy work environments. Ann. 1st. Super. Sanita 9 (Spec. Number 1): 383–388. Chem. Abs. 83:47621. (Ital.).

Gases and vapors fixed (adsorbed) on the surface of (or absorbed into) dust particles could add to the toxicity of dust exposure.

Formaldehyde, which usually limits its action to the upper respiratory tract (D5, D14) reaches the lungs if fixed on respirable dust particles.

Comment: In addition to the above mechanism, ingestion of polluted dust particles, or the swallowing of bronchial phlegm containing such particles, can result in direct gastrointestinal exposure (D5) to HCHO. Formaldehyde is a strongly sorbed substance; see Section C and C36. And as pointed out (D4, p. 137), the introduction of particulates with a tumorigenic agent appears to increase the likelihood of a positive outcome; formaldehyde is listed (D11a) as a suspected carcinogen of the lung (D11b).

D17. Pavlenko, S. M., and V. A. Guseva
1973. Dynamics of the development of adaptive reactions under the long-term effect of industrial poisons entering an organism by different means. Itogi Nauki Tekh., Farmakol,, Khimioter. Sredstva, Toksikol., Probl. Toksikol. 5:110-119. Chem. Abs. 83:109347. (Russ.).

During long term poisoning with formaldehyde--for example, by inhalation--adaptation reactions occurred earlier than for poisoning by oral administration. Poisoning by combined inhalation and ingestion resulted in the earliest reactions. The activity of the central nervous system was observed to occur in cycles of several months' duration.

D18. (a) Baer, R. L., D. L. Ramsey, and E. Biondi
1973. The most common contact allergens: 1968-1970. Arch. Dermatol. 108(1):74-78.

(b) Epstein, E., W. Rees, and H. Maibach
1968. Recent experience with routine patch test screening. Arch. Dermatol. 98(1):18-22.

(c) Baer, R. L., G. Lipkin, N. B. Kanof, and E. Biondi
1964. Changing patterns' of sensitivity to common contact allergens. Arch.. Dermatol. 89(1):63-68.

(d) Rostenberg, A., Jr., and M. B. Sulzberger
1937. Some results of patch tests. Arch. Dermatol. 35:433-454.

These four papers represent changes which have taken place in the population index of Sensitivity to different contact allergens, Thus, in the period 1937 to 1961/1962, the index of sensitivity to formaldehyde increased 290 percent (D18c). And more recently (D18a), HCHO was listed as one of the 10 most common contact allergens.

D19. Ivanova, T. P., N. K. Statsek, A. I. Buslenko, and others
1973. Sensitizing action of formaldehyde. Farmakol. Toksikol. (Kiev) (8):161-163. Chem. Abs. 80:116846. (Russ.).

Animals showed an allergenic reaction to formaldehyde applied to the skin. In humans, there were symptoms of a sensitizing action which resulted in changes in the blood system. See also D12.

D20. (a) Technology Review
1973. More than one hazard in smoke. Technol. Rev. 76(2):66.

(b) Zikria, Bashir A.
1973. Smoke poisoning in fires. 166th National Am. Chem. Soc. Meeting, Chicago, Ill. August, 1973. Division of Polymer Chemistry Abstract: Poly 58., ACS, Washington, D.C.

(c) Zikria, Bashir A.
1972. Inhalation injuries in fires. Appraisal Halogenated Fire Extinguishing Agents, Proc. Symp. p. 42-52. Nat. Acad. Sci., Washington, D.C. Chem. Abs. 78:93311.

In a study of toxicity of smoke from fires (including cigarettes), the author (D20a) believes aldehydes may be the cause of fatalities not due to CO. Furthermore, the effects of aldehydes on the cells are cumulative for long or repeated exposures. He postulates (D18b, D18c) that the short chain aldehydes react with the amino acids and RNA of respiratory tissue cells causing denaturation of cell proteins and consequent damage to pulmonary cell tissue.

D21. Rosenkranz, H. S.
1972. Formaldehyde as a possible carcinogen. Bull. Environ. Contam. Toxicol. 8(4):242-244. Chem. Abs. 78:80636.

In addition to the fact that formaldehyde has been known, from literature citations, to be a mutagen, the author now believest it to be a potential carcinogen. Using a microbial assay method, he has shown it to behave similarly to other known carcinogens. Exposure to low concentrations for long periods of time is a situation which probably increases the chance of carcinogenesis.

D22. U.S. Department of Labor, Occupational Safety and Health Administration
1971. Subpart G--Occupationalhealth and environmental control, 1910.93 Air comtaminants (gases, vapors, fumes, dust, and mists). Fed. Regist. 36 (105, May 29) :10503-10504.

The official Federal (OSHA) notification that exposure to formaldehyde (by inhalation, ingestion, skin absorption, or contact) shall be limited to a maximum TLV = 3 ppm (8-h time-weighted average). Above this concentration, exposure shall be avoided, or protective equipment provided and used, See D3, D23.

D23. Feldman, Y. G., and T. I. Bonashevskaya
1971. Action of low concentrations of formaldehyde on the body. Gig. Sanit. 36(5):6-11. Chem. Abs. 75:33270. (Russ.).

Soviet norms for formaldehyde in the atmosphere of inhabited places had been previously set at: (a) single time maximum = 0.035 mg/m^3 (0.03 ppm); (b) constant exposure maximum = 0.012 mg/m^3 (0.01 ppm). It was recommended that these not be changed. The maximum for industrial areas was set at 0.1 mg/m^3, but rats exposed to this level of HCHO showed changes in the time required for nerve activity and tissue structure. See D3, D22.

D24. Dalhamn, T., and A. Rosengren
1971. Effect of different aldehydes on tracheal mucosa. Arch. Otolaryngol. 93(5):496-500.

A study of tracheal tissue showed that formaldehyde appeared to be the most ciliotoxic, followed by acetaldehyde and acrolein. Their experiments largely confirmed the results of other authors. Data for HCHO indicated that ciliotoxicity increased rapidly for small increases in the concentration of vapor.

D25. Schorr, Wm. F.
1970. Allergic skin reactions from cosmetic preservatives. Am. Perfum. Cosmet. 85(3):39-41, 45-47. Chem. Abs. 72:124977.

The allergenic properties of cosmetic preservatives (including HCHO) are reviewed, The extensive use of formaldehyde in various products and processes markedly increases human exposure and produces greater risk (D18c).

Comment: Certain aspects of formaldehyde allergy as regards the public on the whole appear important to the "formaldehyde problem" in particleboard use. The increased exposure incidence carries with it the probable decreased tolerance as more people become sensitized (D18). Such has happened already with mercury compounds (antibacterial agents), as Schorr points out.

D26. Akabane, J.
1970. Aldehydes and related compounds. Int. Encycl. Pharmacol. Ther. 20 (Alc. Deriv., v2):523–569. Chem. Abs. 76:108760.

A review of the metabolism, toxicity, and pharmocological effects of lower aliphatic aldehydes, especially formaldehyde and acetaldehyde. 190 literature references.

Comment: With respect to the increasingly stringent requirements of OSHA and the results of more recent research on the toxicity of formaldehyde, some of the data in Akabane's paper are out of data. The report is, however, weighted more (about 2–1/2 times) in favor of acetaldehyde than of formaldehyde.

D27. Nefedov, Y. G., V. P. Savina, N. L. Sokolov, and others
1969. Contaminants in the air exhaled by man. Kosm. Biol. Med. 3(5):71–77. Chem. Abs. 73:101783 (Russ.).

Both formaldehyde and acetaldehyde were found in the air exhaled by healthy people in the age range of 25 to 35 years. and may be regarded as normal metabolites in mammals (D26).

D28. Sgibnev, A. K.
1968. Effect of low formaldehyde fume concentrations on humans. Gig. Tr. Prof. Zabol. 12(7):20–25. Chem. Abs. 70:14218 (Russ.).

The basic physiological functions of humans were examined experimentally at several concentrations of formaldehyde gas. At 1.0 mg/m^3 (0.83 ppm) all subjects suffered an orientation reaction, olfactory sensation, and in the most susceptible individuals an irritation of the upper respiratory tract. At 0.3 to 0.4 mg/m^3 (approximately 0.3 ppm) the majority of subjects exhibited an orientation reaction, and half of them an olfactory sensation after exposure for: 10 minutes at 1 mg/m^3, the majority showed accelerated breathing and electroencephalogram changes; at 0.3 to 0.4 mg/m^3. there were no substantial changes in recorded functional indicators.

Comment: These observations agree with those of Freeman and Grendon (B32) where HCHO at 1 ppm (1.2 mg/m^3) was found objectionable, and the subjective effect of the odor upon employee performance was noted. The effect of formaldehyde on human physiology has been summarized earlier in the following-citations: D7b, D8, D10, D12a, D12f, D12g, D12h, D15, D18 D25.

Section E. Odor and Odor Control

E1. Jonas, L. A., and J. M. Eskow
1976. Survey of new sorbents for application to protection devices. Dept. of the Army, Edgewood Arsenal, Aberdeen Proving Grounds, Md. March, 26 p.

Adsorbent: A cooperative study between the United States and the United Kingdom in the application of sorbents to protection and air-monitoring devices. The protection devices are the type that use sorbents for air purification. The survey included a comprehensive survey of the literature.

E2. Hunt, C. M., and D. M. Burch
1975. Air infiltration measurements in a four-bedroom townhouse using sulfur hexafluoride as a tracer gas. U.S. Department of Commerce, Natl. Bur. of Stand. Wash., D.C., 16 p.

Ventilation: A four-bedroom house was contained in an environmental chamber with control over both the inside and outside temperature with essentially no wind velocity. The SF_6 tracer gas measurements were compared with air exchange rates imposed on the house by means of a fan. Also investigated was the effect of sealing doors and ducts.

Comment: Data obtained should be complementary to that cited earlier (A3, A23). Accurate ventilation rates for occupied structures (see E5, E9), plus accurate values for the rate of emission of formaldehyde from various types of adhesive-bonded wood-panel materials, would permit a ventilation engineering evaluation of the habitability of a formaldehyde-contaminated space. Corrective measures could be more suitably designed for the severity of the problem. See also C34.

E3. Worthy, Ward
1975. IITRI work focuses on chemistry of smell. Chem. Eng. News 53(5):19-20.

Odor: IITRI is the Illinois Institute of Technology Research Institute. The major effort at the odor science center is in developing "chemical signatures" associated with odors. The human sense of smell can detect as little as 0.1 ppm in air of some compounds, but thresholds vary with individuals, Four "sensory dimensions" are considered in measuring odors: detectability (the only one, so far, regulated by statute), intensity, character, and "the hedonic dimension"--the pleasantness or not of an odor. Odor detection is highly subjective, See also E8.

E4. Kyle, B. G., and N. D. Eckfioff
1974. Odor removal from air by adsorption on charcoal.
EPA/650/2–74/084. Kansas State Univ., Manhattan, Kan.
Sept. 109 p.

Adsorbent: Fixed–bed adsorption studies were carried out for two organic vapors: ethylmercaptan and acetaldehyde. The latter could be 98 percent removed from air containing the vapor in the 10-to 35-ppm range.

Comment: Because of the difference in boiling points between acetaldehyde (21° C) and formaldehyde (–19.5° C, a gas at room temperature), the latter would be less efficiently removed (E5, p. 33.4; see also Section C). In fact, Lee (E12) showed that the capacity of straight activated charcoal varied with RH. See E10 for information and data from measurements made at concentrations of 1 to 15 ppm.

E5. American Society of Heating, Refrigerating, and Air–conditioning Engineers, Inc.
1973. Odor Control. Handbook and Product Directory:
1973 Systems. Ch. 33, p. 33–1 to 33–12. ASHRAE, New York.

Odor Control: The two principal sections discuss: (a) Odor control methods and (b) costs. The former is subdivided into the following topics:
Removal by ventilation
Removal by washing and scrubbing
Control by adsorption
Control by chemical reaction
Control by combustion
Odor masking and counteraction
Control by masking
Control by counteraction
Portable units.
See also E13, and E15 in particular.

E6. American Society of Heating, Refrigerating, and Air–conditioning Engineers, Inc.
1972. Odors. Handbook of Fundamentals. Ch. 11, p. 187.
ASHRAE, New York.

Odor: A technical discussion of odors and odor technology. The section on odor removal is brief, but informative. The topics are more fully covered in E5.

E7. Diaper, E.W.J.
1972. Ozone--practical aspects of its generation and use; I, Generation. Chem. Technol. 2(6):368-375; II, Use. Chem. Technol. 2(8):498-504.

Odor Control: A review of ozone aimed at industrial usage. In a brief discussion of odors (Part II), ozone at 1 to 2 ppm is said to be effective against organic odors, with contact time of a few seconds to half a minute.

Comment: The viewpoint in E6 is that ozone's effect is to reduce sensitivity (see E16 of the sense of smell rather than the odor concentration, Furthermore, the amount of ozone required for air deodorization would be too high for human occupancy. The official threshold limit value has been set (D22) at 0.1 ppm. See E15 for an extensive discussion of the use of ozone for odor control by means of ultraviolet radiation (lamps). Table 85 (E15) details the biological effects of ozone.

E8. American Society for Testing and Materials
1971. Standard method for measurement of odor in atmospheres (dilution method). ASTM Standard Desig. D 1391-57. ASTM, Philadelphia, Pa.

Odor: A standarized procedure intended to establish a quantitative concept of odor whereby the relative quantities of odor from one or more sources can be compared. The test depends upon the human olfactory sense for measurement, hence is highly subjective. The threshold of detection is determined by utilizing progressive dilution of the odor source with odor-free air.

E9. American Society of Heating, Refrigerating, and Air-conditioning Engineers, Inc.
1970. Ventilation of the industrial environment. Guide and Data Book: Systems. Ch. 19, p. 287. ASHRAE, New York.

Ventilation: A comprehensive list of the requirements for control of the industrial environment. The section "Control of environmental gases and vapors, dusts, and fumes" details calculations for design of dilution (ventilation) systems. See E13 also.

E10. Stakavich, A. J.

1969. The capacity of activated charcoal under dynamic conditions for selected atmospheric contaminants in the low parts-per-million range. Am. Soc. Heat. Refrig. Air-cond. Eng., Inc. Symposium: "Odors and odorants: The engineer's view," p. 49. [Chicago, Ill. Jan. 27-30, 19691 ASHRAE, New York.

Adsorbent: Data are reported for dynamic adsorption of formaldehyde in the concentration range of 1 to 15 ppm. From this and data for other organic solvents, the author found the actual usable capacity of charcoal for odor removal was very dependent upon odor threshold and odor characteristic (see E8), Published capacity data are more often based on higher concentration levels than those tolerated by or safe for human occupants. In addition, capacity is dependent upon temperature and relative humidity (E12).

Ell. Hanna, G. F., and J. Richardson

1969. A solution for industry odor problems. Am. Soc. Heat. Refrig. Air-cond. Eng., Inc. Symposium: "Odors and odorants: The engineer's view." p. 57, [Chicago, Ill. Jan. 27-30, 19691 ASHRAE, New York.

Adsorbent: A discussion of the alumina-permanganate air purification system with examples, including formaldehyde. The active solid is alumina which has been impregnated with a soluble permanganate solution (e.g., potassium permanganate) and dried (E14). The authors cite as an example, a textile mill room where the aim point for HCHO was 0.25 ppm or less in order to achieve freedom from irritation.

Comment: A solid reactive chemical as described, activated carbon, or other adsorbent type materials (see Section C) would be suitable for use in portable self-contained units discussed in reference E5.

E12. Lee, D. R.

1965. Using impregnated activated carbon, J. Am. Assoc. for Contamination Control 4 (Dec):18,19,21.

Adsorbent: Straight activated charcoal has high sorptive capacity for many different air contaminants. It varies, however, in its ability to retain formaldehyde, due principally to variations in relative humidity, capacity being very low at low relative humidity, No data are given. The use of an impregnated charcoal eliminates much of the effect of RH in removing HCHO from air.

E13. Viessman, W.
1964. Ventilation control of odor. Ann. N.Y. Acad. Sci. 116(2): 630-637

Ventilation: Odor control by ventilation is limited, but is usually the simplest method. Details are given for calculating air exchange requirements commensurate with various situations. See also <u>E5</u>, <u>E9</u>.

E14. Hanna, G. F., R. L. Kuehner, J. D. Karnes, and others
1964. A chemical method for odor control. Ann. N.Y. Acad. Sci. 116(2):663-675. Chem. Abs. 61:11640.

Adsorbent: The alumina-permanganate absorber pellet (<u>E11</u>) is described in technical detail, Design factors for an air purifying system are discussed and illustrated. Factors determining the life of the deodorant system are discussed.

E15. Summer, W.
1963. Methods of air deodorization. American Elsevier, New York. p. 308.

Odor Control: A comprehensive review of air deodorization. In addition to the engineering fundamentals needed to combat air pollution, the psychophysiological aspects of odors and the sense of smell are presented.

E16. Elonka, S.
1961. Five ways to keep indoor-air odor-free. Power 105(2): 178-179.

Odor control: The five methods discussed (briefly) are: (1) Activated carbon, (2) air sterilization (using ultraviolet-ray lamps), (3) ozone, (4) washing filtered air, (5) dilution of inside air. The author's view of ozone is that it masks odors because of its pungent smell similar to chlorine (<u>E6</u>). Because of the low toxic level for humans (<u>D22</u>), the author "suggests" limiting concentrations to 0.01 to 0.05 ppm. However, ozone is not too effective as either a masking or sterilizing agent at these low concentrations. See also <u>E6</u>, <u>E7</u>.

APPENDIX: ABBREVIATIONS

ASHRAE	American Society for Heating, Refrigeration and Air Conditioning Engineers, Inc.
ASTM	American Society for Testing and Materials
Bulg.	Bulgarian
Chem. Abs.	Chemical Abstracts
Czech.	Czechoslovakian
Dan.	Danish
Enq.	English
EPA	Environmental Protection Agency
	Gram
Ger.	German
GC	Gas chromatography
GLC	Gas – liquid chromatography
HCHO	Formaldehyde
Ital.	Italian
Jap.	Japanese
m: m^3	Meter: cubic meter
mg	Milligram--one thousandth of a gram
MOE	Modulus of elasticity
MOR	Modulus of rupture
MW	Molecular weight
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Act.
pct	Percent
PF	Phenol-formaldehyde
ppm	parts per million
RH	Relative humidity
Rom.	Romanian
Russ.	Russian
TLV	Threshold level value
UF	Urea – formaldehyde
UV	Ultraviolet
Sec.	Second
μg	Microgram--one millionth of a gram

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