

# Visual Method for Measuring Formaldehyde Release From Resin-Bonded Boards

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## Abstract

An alkaline solution of purpald absorbs formaldehyde vapor quantitatively from air and turns purple. Under standard conditions, the intensity of the color can be used to measure release of formaldehyde from particleboard or fiberboard bonded with urea-formaldehyde or phenol-formaldehyde resins. An airflow test and a spot test using purpald are outlined; these tests can be used for grading boards or for determining satisfactory curing. Because of their simplicity and rapidity, these tests could be used routinely or in spot checks in board manufacturing plants.

ONE OF THE MAJOR DRAWBACKS to more widespread use of particleboard and fiberboard in building construction and furniture manufacture is the gradual but continuous release from some boards of small amounts of formaldehyde. This formaldehyde arises from free or loosely bound aldehyde in uncured residues of the phenol-formaldehyde or urea-formaldehyde resins used in their manufacture (5-7, 12). In confined or poorly ventilated areas—for example, in drawers, cabinets, closets, trailers, or mobile homes—the buildup of formaldehyde vapor released from poor-grade boards or panels can become so heavy that its unpleasantly pungent odor becomes intolerable to humans. A health hazard may even be associated with higher concentrations of formaldehyde (6, 7, 12, 14). Removal or exchange of the boards may sometimes be required. Consequently, there has been a growing reluctance by the building and woodworking trades to risk the use of particleboard or fiberboard in areas where a formaldehyde buildup problem might occur.

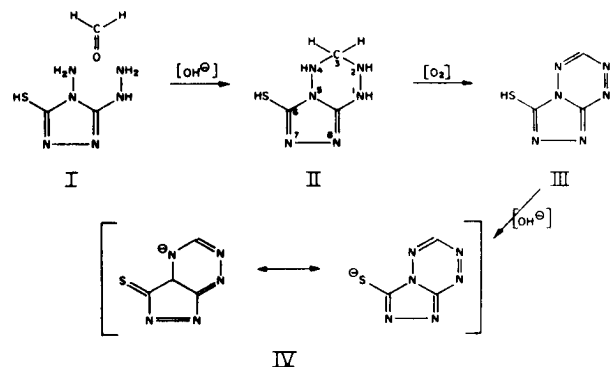
Complete rejection of the boards for use in confined areas is unjustified; not all boards release enough formaldehyde to become objectionable. However, the difficulty lies in our inability to judge which boards may release larger amounts of formaldehyde and thus become unacceptable and which boards are safe to use. It is still not known exactly which parameters or combinations of parameters influence the rate and extent of formaldehyde release from boards. Factors such as the amount of formaldehyde used in the resins, the formulation of the resin, the amount of resin applied, the curing conditions and curing times used, the plate pressures during forming, the duration of storage before use, and the environment and climate in which the final use is made may all affect whether formaldehyde release from a board will be so extensive as to make its use inadvisable (6, 7, 11, 15).

For this reason, board manufacturers are currently unable to predict easily whether their boards will be suitable for use in certain building or manufacturing applications. There is a dire need for a simple and sensitive test for formaldehyde release from boards that can be used as a basis for grading boards and projecting their suitability for diverse application. Some tests have been evolved (1, 4, 7, 8, 10-12), but these are invariably too intricate and time consuming, and because of the aggressive nature of the chemicals required, are often too hazardous for routine use in board manufacturing plants.

## Nature of the New Test

We have now devised a simple test procedure which has none of these objections and which can be conducted by nontechnical personnel in board manufacturing plants. It can be used to obtain crude comparative values for formaldehyde release from resin-bonded plywood, particleboards, or fiberboards. The procedure also forms the basis of a simple nondestructive spot test for routine use on any board leaving a plant or for onsite testing of complaints.

The test is based on the use of a novel reagent for detecting aldehydes (3), 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (I) or purpald®, from the Aldrich Chemical Co., 940 West St. Paul Avenue, Milwaukee, Wisconsin (see Schematic).



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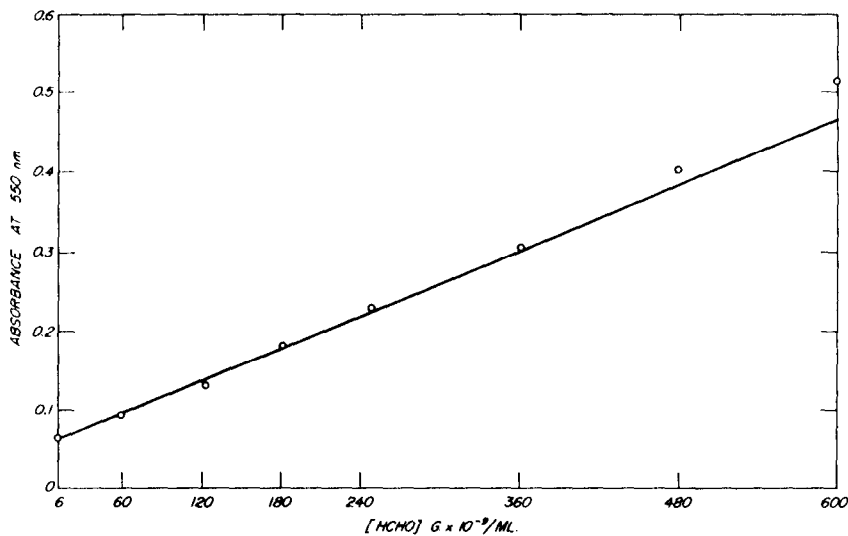


Figure 1. - Beer's law plot [absorbance versus concentration] of the color formed from known amounts of formaldehyde with purpald. The relationship is linear in the range  $6.0 \times 10^{-9}$  to  $6.0 \times 10^{-7}$  grams per milliliter (6 to 600 nanograms of formaldehyde).

Formaldehyde condenses with a solution of this reagent in dilute sodium hydroxide to give 1,2,3,4-tetrahydro-6-mercapto-*s*-triazolo [4,3-*b*]-*s*-tetrazine (II). This is rapidly dehydrogenated by air to produce red-brown 6-mercapto-*s*-triazolo[4,3-*b*]-*s*-tetrazine (III), which gives rise in the alkaline solution to the anion (IV), whose resonance and extended conjugation result in an intense purple color.

The maximum wavelength of absorption ( $\lambda_{\max} = 550 \text{ nm}$ ) and the intensity of the color formed can gradually change. After 1 to 2 days of time the color finally fades unless protected from the air. These changes appear to be due to slow decomposition in air of (IV) and the absorption of carbon-dioxide from the atmosphere, which causes a drop in pH of the alkaline solution and allows reprotonation of the thioxide anion (IV). If the test is performed with solutions of formaldehyde of known concentration and the color produced is measured in a spectrophotometer, strict adherence of Beer's law is not found (Fig. 1) unless precautions are taken. In practice, any assay of formaldehyde with purpald is therefore only approximate. However, if the test is conducted with board samples under standardized conditions, reproducibility

is achieved and valid comparisons can be made between various boards.

#### Airflow Procedure

We have taken advantage of the fact that an air oxidation is needed to produce the color, and have used a stream of air as carrier gas to convey the formaldehyde from the air-dry board sample to the solution. The problem of low absorption efficiency encountered with analysis of formaldehyde in air with another sensitive reagent (2) was not experienced; complete absorption of the formaldehyde from the airstream by the alkaline solution in a single tube was found. The test was conducted as follows (Fig. 2).

Air from a compressed air source was regulated with a valve to a flow rate of 1 milliliter per second, measured with a flowmeter. A small sample of the board to be tested was cut off and fines were obtained from it by drilling holes with a sharp bit on a drill press. The fines were collected immediately in a tightly stoppered bottle. For each test, a 5-gram sample of fines was rapidly weighed out and transferred through a powder funnel into a Nalgene drying tube fitted with a cotton filter at the bulb end. The other

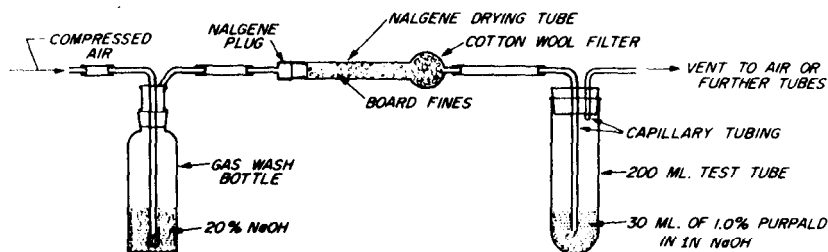


Figure 2. - Setup for test of formaldehyde release from board fines using absorption of vapor in alkaline purpald solution.

end of the tube was closed with a plug fitted with an inlet connection supplied with the tube. The inlet was connected through a trap containing sodium hydroxide solution (to absorb carbon dioxide and any formaldehyde impurity from the air carrier gas) to the air source. The outflow tube was connected to a capillary tube, which was immersed in 30 milliliters of 1.0 percent purpald in 1 N sodium hydroxide contained in a 200-milliliter test tube (38 by 200 mm). The capillary had been fitted into a No. 8 rubber stopper provided with another outlet capillary to allow the carrier air to escape but prevent atmospheric air from entering the tube. The airstream was passed through the system for a suitable time, generally 10 or 20 minutes for good quality boards. The test tube was then stoppered tightly with a No. 8 stopper to prevent CO<sub>2</sub> absorption. The color intensity was compared visually with that produced simultaneously under identical conditions from samples of a standard board of known acceptable quality. The standard board had been presawn into 2- by 2-inch squares which were wrapped in aluminum foil and stored in a refrigerator-freezer to prevent loss of formaldehyde. Fresh drillings were made from one such square for use in a standard test immediately before the test was run.

As mentioned above, a single tube of reagent was sufficient to absorb all the formaldehyde. Purpald solution in second and third tubes connected in series remained completely uncolored during test runs even with boards that released large amounts of formaldehyde and in control tests using an aqueous 1 percent formaldehyde solution in a flask instead of board fines in a tube.

#### **Sensitivity and Alternate Procedures**

The limit of detectability lies around 50 nanograms of formaldehyde in 1 milliliter, to which only one drop of reagent need be added. A pink color is detectable after the solution has stood in a stoppered vessel for a few minutes. Best visual comparisons can be made in the 200-milliliter test tubes when amounts of formaldehyde in the range of 100 to 10,000 nanograms have been collected. The only compounds that can interfere with the test are other volatile aldehydes: No other class of organic compounds gives a reaction with purpald.

Alternative methods of running the test can be envisaged. For instance, the length of time required to match a standard color could be measured, but this is not recommended, since the color may take a long time to develop with good boards and since the color maximum for a given amount of formaldehyde is transient. Immersion of board specimens, drillings, or millings directly into the reagent solution generally gave such intense colors from poor boards that only very small samples (5 to 10 mg) were needed. This creates the problem of representative sampling. The technique of extraction of larger samples (0.2 to 0.5 g) with large volumes of water (200 ml), from which small aliquots (1 ml) were taken and added to the reagent solution gave colors of suitable intensity for visual comparison. This could be the basis for a good testing technique, but the leachable amount of formaldehyde is not necessarily the same as that released to air.

The purpald reagent is so sensitive that its alkaline solution will turn pink to purple if exposed to the air in a room containing traces of formaldehyde. Purpald can therefore also be used for detecting formaldehyde *in situ* in places where particleboard or hardboard is in use even at levels below the 0.88 ppm (14) limit of odor detectability or the maximum permissible industrial level (15) of 6 milligrams per cubic meter of air. In consequence, if the reagent were being used in a production plant, it would be necessary to find a test site relatively free of formaldehyde.

A stock solution of the reagent can be conveniently stored in an automatic-zero reservoir buret. The air from the hand bulb used for filling the buret should be passed through a gas wash bottle containing concentrated (e.g., 20 percent) sodium hydroxide to absorb carbon dioxide and formaldehyde vapors. If available, compressed nitrogen is preferable to air. The use of compressed air from cylinders delivered to the plant from an outside source is also preferable for use as the carrier gas for flushing the board fines.

Another test used for assaying formaldehyde in air (2,9) was also applied to board fines but was found to be much less suitable: The reagent is more expensive, color development cannot be watched as it proceeds, problems are encountered with the collection efficiency of the system (2) and with the precipitation of the pigment formed (2), and the color produced is neither as intense nor as stable.

#### **Spot Test Procedure**

The airflow test outlined above is still too time-consuming and complicated for routine application to individual boards. However, purpald solution can also be used in a nondestructive spot test which is so simple and fast that it could be applied routinely to every board being shipped out by a manufacturer. If a drop of 1 percent purpald in 1 N sodium hydroxide solution is smeared on a board releasing formaldehyde, a bright purple color is detectable within about a minute. On boards that show little or no formaldehyde release in the tube test, only a dull brown spot is formed. When the test is conducted in an atmosphere polluted by formaldehyde—for example, in board plants—interference from formaldehyde in the air does not occur for several minutes. The spot test is still reliable under such conditions. The only precaution necessary is that the reagent used in the spot test be protected against formaldehyde absorption while in storage or use.

#### **Model Applications**

Either the airflow test or the spot test can be used as a tool to grade boards. Boards which do not perform satisfactorily in the spot test can be double-checked in the more accurate airflow test. If their rate of formaldehyde release is too high, such boards can be subjected to further heat curing or kept stored in a well ventilated area until excess formaldehyde has all escaped. Both tests can also be used to assess the efficacy of curing resin-bonded boards.

As a demonstration of this, three boards of identical composition were prepared. One was submitted to a

standard cure, another was undercured, the third was overcured. All three boards gave bright purple colors in the spot test immediately after manufacture. Samples cut from the freshly prepared boards were wrapped in foil and stored in a freezer; drillings from these samples were subjected to the airflow test the next day. Every 500 seconds, an aliquot was withdrawn temporarily from the tube and the color intensity measured as absorbance at 550 nanometers. From the curves obtained (Fig. 3), it is apparent that the rate of formaldehyde release from the overcured board was much lower than that from the board given the standard cure, whereas the release from the undercured board was faster.

After the boards had been exposed to the air for 1 week, the airflow tests were repeated. The rate of formaldehyde liberation was still lower from the overcured board than from the standard-cured board. However, the rate was then lowest for the undercured board. This board was so weak that it delaminated during drilling. Although it started out with the highest level of free formaldehyde, its greater porosity must have allowed the excess formaldehyde to escape more easily and more rapidly.

In the spot test, the undercured board still reacted strongly, the standard-cured board gave a weak purple,

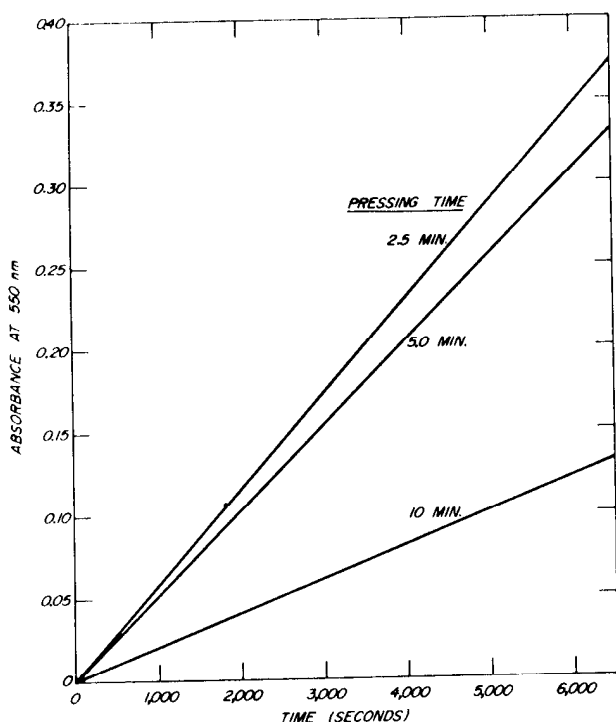


Figure 3. - Absorbance at  $\lambda_{max}$  (550 nm.) versus time of the color produced in the airflow test with purpald by formaldehyde released from three urea-formaldehyde resin-bonded boards cured for various times. The boards were made from 1.00- by 0.030-inch flakes of Douglas-fir bonded with 6 percent urea-formaldehyde resin and had a density of 40 pounds per cubic foot. The platen temperature was 325° F, the boards were pressed for 1) 2.5, 2) 5.0, and 3) 10.0 minutes. The 5-minute cure is the customary standard cure for such boards. The tests were run within 24 hours of board preparation.

and the overcured board a very weak purple. This reflects the fact that purpald reacts slowly with free hydroxymethyl (methylol) groups, as was shown in tests with formaldehyde-free N, N'-bis-hydroxymethylurea. Although after 1 week the undercured board had the least residue of free formaldehyde, it still contained the largest amount of uncured hydroxymethyl groups.

The airflow test can also be adapted to monitor air quality in board manufacturing plants. An air sampling device can be conveniently used to draw a definite volume of air through a sintered glass filter (Porosity A) into a measured volume of reagent in an air-sampling midget bubbler (13). The purple color produced can be compared with standards or measured spectrophotometrically and the formaldehyde content derived from the calibration curve (Fig. 1).

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