Health & Safety

EPA Final Risk Evaluation for Methylene Chloride

Methylene chloride, a once-common ingredient in commercial paint strippers used in conservation, has been the subject of a series of restrictions over the past few years due to health and safety concerns. In July 2022, the EPA released a draft risk evaluation for methylene chloride which proposes that methylene chloride presents an unreasonable risk to human health. After receiving public comment and publishing a final version, the EPA will introduce further regulations to limit the manufacture, distribution, and disposal of methylene chloride (EPA 2022a).

The EPA considered hazards and exposure, magnitude of risk, exposed population, severity of the hazard, uncertainties, and other factors in making this determination. In their assessment, the EPA evaluated the effects of methylene chloride on workers, occupational non-users (individuals nearby who were not using the material directly), consumers, and bystanders (EPA 2022a). 52 out of the 53 evaluated conditions of use in industrial, commercial, and consumer contexts were demonstrated to cause an unreasonable risk to human health. All consumer uses of methylene chloride were found to cause unreasonable risks, including use as solvent, in adhesives, in brush cleaners, an as adhesive and caulk removers. The primary health risks identified for methylene chloride were neurotoxicity from short-term exposure and liver effects and cancer from long-term exposure (EPA 2022b, 6). The primary routes of exposure were inhalation and dermal exposure. Methylene chloride is highly volatile and can have severe health effects with short term exposure (under 1 hour); this was a key consideration in the EPA's evaluation of the level of risk (EPA 2022b, 8). The EPA did not find any unreasonable risks to the environment in any evaluated conditions of use.

The findings of the 2022 EPA risk evaluation demonstrate that conservators should discontinue the use of methylene chloride. Disposal methods vary by state; local regulations should be consulted for more information.

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Meet Your Match: Storage of Matches in Collections

Conservation professionals may encounter any number of hazardous materials in collections. Items that are familiar from household use may at first seem innocuous, but on second glance warrant additional attention to mitigate health and safety risks in a collections setting. Matches, occasionally found in museum collections and archives, are one such example. Questions about health and safety risks associated with matches, particularly concerning their flammability, have been the subject of several blog posts and discussions on professional forums in recent years. This article attempts to address some of these open questions by examining the risks associated with chemicals used historically in the matchmaking industry and proposing best practices for storage.

A Brief History of the Match Industry

Early matches evolved in Europe during the Industrial Revolution as demand increased for an easily accessible non-mechanical fire starter. After the discovery of phosphorus by Henning Brandt in 1669, numerous individuals began creating matches using various recipes and formats (Crass 1941, 116). In addition to potassium chlorate, sulfur, paraffin, and gum arabic, many of these early matches utilized white phosphorus (also called yellow phosphorus or tetra-phosphorus, P_4) as a reactive agent. Working conditions in nineteenth-century match-making factories were poor and provided no ventilation from white phosphorus fumes, which had severe repercussions on human health. Factory workers developed "phossy jaw," which involved disintegration of the jawbone and permanent disfiguration of the face (Satre 1982, 9). White phosphorus was also incredibly toxic when ingested and could spontaneously combust, leading to many workplace accidents (Finch and Ramachandran 1983, 22, 23; Lee 1966, 13). These poor working conditions prompted the London matchgirls strike of 1888, largely considered one of the earliest events driving the development of factory labor regulations in Europe (Satre 1982, 8).

Safety matches using red phosphorus, a safer alternative to white phosphorus, on a specially prepared striking surface were developed by the 1850s; however, matches made with white phosphorus remained popular throughout the nineteenth century due to their lower cost and ease of use (Satre 1982, 11; Thorpe 1899, viii). The Berne Convention of 1906 resulted in a treaty requiring countries to prohibit the use of white phosphorus in the manufacture of matches; the material was phased out of manufacture throughout Europe and the United States in the following decades; see Table 1 (Lee 1966; Charnovitz 1987, 571).

Table 1. Legislation restricting or prohibiting the use of white phosphorus in the manufacture of matches (data from Lee 1966 and Myers and McGlothlin 1996).

Country	Date	Type of restriction
Sweden	1870	Allowed only under strict regulations
Finland	1872	Total ban
Denmark	1874	Total ban
Russia	1892 (tax established); 1905 (tax doubled)	Tax; by 1906 one in 50 matches produced contained white phosphorus
France	1897	Total ban
Berne Convention (Finland, Denmark, Switzerland, Luxemburg, Italy, Holland, Germany)	1906	International ban
Great Britain	1910	Total ban
United States	1912-1914 (legislation passed 1912, importation prohibited 1913, exportation prohibited 1914)	White Phosphorus Match Act of 1912 – required manufacturers to register, pay a tax, and affix revenue stamps to match boxes. Violations were punishable by fine and prison term.
India	1919	Total ban
Japan	1919	Total ban
China	1925	Total ban

Much like many early matches, the coated tips of today's safety matches contain an oxidizing agent, typically potassium chlorate, in addition to additives such as glue, sulfur, and ground glass (Corbridge 1990, 63). However, safety matches require friction against a specially prepared striking pad (typically present on the packaging), which contains red phosphorus. The separation of the two reactive agents between match head and match box means that safety matches are less prone to accidental ignition. Modern strike-anywhere matches contain two reactive agents (typically phosphorus sesqui-sulfide and potassium chlorate) on the match head, meaning that the combustion reaction can take place with friction against any hard, rough, and dry surface (Corbridge 1990, 107).

Strike-anywhere matches pose a greater flammability risk and are also subject to more restrictive transport and shipping regulations in the United States (USPS 2022). They are easily recognizable by their two-toned head, whereas safety matches have a single-color tip (Figure 1). The exception to this is modern stormproof matches, which have a two-toned head but require a special striking pad. Stormproof matches typically have a thick coating that extends further up the shaft of the matchstick than typical safety or strike-anywhere matches.

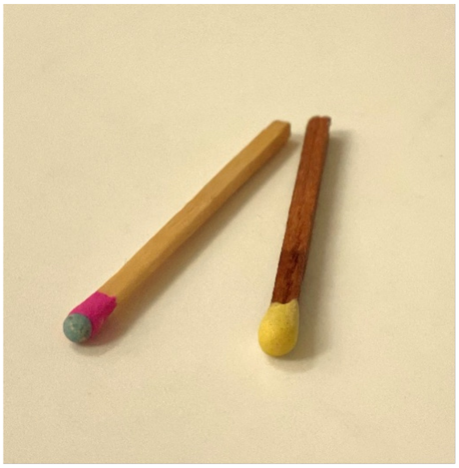

Figure 1. A strike-anywhere match (left) and safety match (right).

Health and Safety Considerations of Common Match Components

White Phosphorus (Early Matches)

Early matches made with white phosphorus pose the greatest health and safety risks in a collections setting. White phosphorus is extremely toxic and is readily absorbed by the body through ingestion, inhalation, and skin contact (CDC 2021). These effects were commonly encountered by factory workers in the nineteenth century working with large volumes of white phosphorus in liquid and vapor form, but such risks are very low in the museum environment where conservation professionals may encounter small quantities in solid form. Toxicity risks can be further minimized through the use of nitrile gloves during handling. The main health and safety risk posed by white phosphorus in a collections setting is its flammability: it can spontaneously ignite at temperatures above 30°C (86°F). It is also highly reactive with many compounds including oxidizers, halogens, some metals, nitrites, and sulfur (CDC 2021).

Red Phosphorus (Early and Modern Matches)

Red phosphorus does not pose the same level of flammability risk as white phosphorus and is non-toxic when ingested (Corbridge 1990, 63). However, in a moist environment red phosphorus can form phosphine gas (PH_3), which is spontaneously flammable in air at 38°C (100.4°F), a temperature that could feasibly occur in collections located in warm climates with no climate control. It is highly reactive with oxidizers (Finch and Ramachandran 1983, 125; Airgas 2020).

Phosphorus Sesqui-sulfide (Strike-Anywhere Matches, 20th c. Onward)

Phosphorus sesqui-sulfide has an auto-ignition temperature of 100°C (212°F). Although this temperature is unlikely in a collections setting, it can be ignited by friction or static discharge. It oxidizes in air, becomes acidic over time, and is highly reactive with oxidizers. It is toxic when ingested (Finch and Ramachandran 1983, 127, 128).

Potassium Chlorate (Early and Modern Matches)

Potassium chlorate is a strong oxidizing agent. It is sensitive to shock and friction and is toxic when ingested. Mixtures containing over 50% potassium chlorate (as is the case with typical match heads) should be considered a fire hazard (Finch and Ramachandran 1983, 120).

Other Ingredients

Match heads are typically formulated with some type of binder to adhere the coating to the match head along with other additives, which vary in type and concentration over time and between manufacturers. Other common ingredients used in matches throughout history, such as sulfur and paraffin wax, are also flammable.

Because the color of match heads does not necessarily correspond with the type of phosphorus used as a reactive agent, identification of white phosphorus in matches is not possible without analytical techniques that are inaccessible to most institutions. Therefore, where provenance is available, conservation professionals should treat all matches produced before the dates listed in Table 1 as if they contain white phosphorus. However, any matches containing white phosphorus in existence today have persisted over a century, presumably through a range of environmental conditions, without igniting; it stands to reason that they are unlikely to do so, likely due to natural degradation of the materials. Regardless, even in small quantities white phosphorus can potentially worsen a fire in collections storage, creating more catastrophic damage. A level of caution is also warranted for modern matches, whose main ingredients pose flammability risks as well. While there is no cause to immediately deaccession matches from collections, conservation professionals should take some basic precautions when preparing matches for storage.

Storage Precautions for Matches in Collections

Colleagues surveyed on the FAIC Global Conservation Forum (DistList) reported institutional practices of removing the heads from matches stored in collections due to concerns over flammability risks; several blog posts report that this practice has a long-standing history in collections settings (Lockshin 2013; Williams 2018). In the industrial hygiene sphere, the first measure of response to a hazardous material is elimination of the hazard. However, this concept is often contrary to fundamental principles of preservation when dealing with hazards that are inherent to collections items. Conservation professionals can instead consider other control measures to minimize risks associated with storing matches in collections including climate control, containerization, and coatings.

For the storage of any type of match, climate control is an important measure of risk mitigation. This is especially the case for matches suspected to contain white phosphorus, which has an auto-ignition temperature of 30° C (86° F). Low relative humidity will minimize the risk of combustion for white phosphorus and prevent the formation of phosphine gas in matches containing red phosphorus. If climate control is not available, conservation professionals can consider the use of a microclimate using conditioned silica gel and/or oxygen scavengers; however, these solutions require long-term maintenance that is often not feasible for many institutions and can result in dangerously rapid environmental changes when neglected. Storage in a dry area away from heat sources and sunlight may be the best option.

To minimize the risk of aggravating a fire, all types of matches should be housed in a container composed of a non-flammable material such as metal. If climate control is not available, glass may be a better alternative to minimize temperatures inside the container. Containers should be labeled with the appropriate GHS flammable symbol and a description of their contents (Figure 2). If the matches are loose, additional housing measures with non-flammable materials should be taken to ensure that they are secure enough to prevent accidental friction during handling and movement. As with any hazardous substance, a higher volume of flammable material causes a greater concern for risk; these risks can be mitigated by limiting the number of matches in each storage container. Matches of any type should be stored away from oxidizers and other flammable materials. Additionally, because sulfur is a common ingredient in match heads, matches should be stored away from materials sensitive to sulfur, such as silver.

Figure 2. The GHS flammable symbol

Finally, conservation professionals can consider coating match heads as a measure to minimize flammability. One blog post reports satisfactory results from coating historic matches with Golden brand Matte Medium. In tests on modern matches, three acrylic adhesives were successful in inhibiting the ignition properties of modern matches; Golden Matte Medium created the least amount of gloss of the adhesives tested (Williams 2018). Coating match tips may also mitigate issues caused by adhesive failure, which can cause match heads to crumble over time (Lockshin 2013).

Conclusions

Though a common household item, matches are composed of materials that pose a flammability risk and can aggravate a fire emergency in a collections setting. While matches are unlikely to spontaneously ignite, precautionary measures to minimize friction, changes in humidity and temperature, and exposure to other flammable materials are warranted. These precautions are especially merited when housing matches manufactured before the widespread ban of white phosphorus as a reactive agent.

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