

PHOSPHORUS SESQUISULPHIDE POISONING

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RECENTLY, two cases of dermatitis of the face due to sensitivity to friction matches were briefly reported.¹ Because of further investigation and thought, the first case of that report is again described. A second case of this kind which has given valuable information as to the etiology of the disease is now added. The ordinary type of match dermatitis as seen in males shows an eczematous dermatitis on the thighs from contact with pockets saturated with match tip material, and occasional involvement of the face is seen as a secondary phenomenon. It should be emphasized here that the cutaneous manifestations in these two cases occurring in females are the result of a primary sensitization about the eyes and face.

CASE 1

Mrs. R.B., age 61, in 1933 had a severe recurring oedematous dermatitis over a period of twelve months about the eyes and face for which a cause was not found, in spite of a good deal of investigation. At or about the same time, she developed a marked loosening of many teeth and as it was thought that pyorrhœa might be a possible cause although no caries was present, these were all extracted. Her teeth had practically no fillings and had been exceptionally good. The facial condition gradually disappeared although there occurred at times some slight dermatitis with itching about the eyes.

About 1941 she again began to get attacks of oedematous dermatitis about the eyes and face which gradually increased in severity and frequency particularly during the past four years. These attacks, which lasted five to ten days, were accompanied by prostration, a marked vertigo, loss of appetite, nausea, and vomiting, necessitating bed rest and absolute quiet. A great deal of medical and dermatological investigation over these years again failed to reveal a cause.

In March 1950, a chance remark by the patient led to the real cause being found—"I would even give up smoking if I could get rid of this". A patch test with a friction match applied to the forearm gave a rather delayed reaction but one which persisted through several weeks. With this clue, on giving up matches and using a lighter for the past year, she has been perfectly well and free from all local and systemic symptoms. She is only a very moderate smoker. Patch tests done with a safety match and with the friction side of a safety box were mildly positive in forty-eight hours.

CASE 2

Mrs. D., age 31, presented a recurring dermatitis about the eyes, of nine months' duration. There was oedema, redness, and itching about both eyes and cheeks, characterized by periods of exacerbation and quiescence. She said that at times her eyes had been itchy without any eruption over the past four years. She was a free lance professional model and this was then a real disability. Treatment had been hitherto ineffectual. She was a smoker and also was fond of striking matches, but not with her nails. A patch test in her case with a match tip gave a vesicular reaction within twenty hours. Later, separate patch tests with the tip and the blue portion of the tip were also positive, the reactions being still very evident at the end of three weeks. Patch tests also

done with a safety match tip and with the friction surface of the safety box were slightly positive. She promptly cleared up on discontinuing the lighting of matches.

In the past two years she had had some loosening of both upper and lower teeth, for which condition other causes were ascribed. In the past three months since refraining from the use of matches, this process, particularly as it affected her lower teeth, has become definitely improved as verified by her dentist.

She further stated that transitory attacks of dizziness had occurred at times and volunteered the information that she had often noted that sneezing occurred with the first puff of a cigarette (nasal allergy).

Dermatologists not infrequently see cases of eczematous dermatitis in females who give a history of a marked exacerbation of the inflammatory process prior to menstruation so that such cases have sometimes been ascribed to menstrual changes. It is recorded here, that in Case 2 prior to and during three successive menstrual periods, the area on her chest at the site of the original patch test became inflamed and itchy, subsiding completely in the intermenstrual period.

Further investigations and comments.—Investigation of these cases therefore has shown (1) positive patch tests with the whole match tip (containing phosphorus sesquisulphide P_4S_3 and other components); (2) positive patch tests with the ignition (phosphorus sesquisulphide) and also the burning portion of the tip (contains sulphur, potassium chlorate, and other components) probably due to traces of phosphorus sesquisulphide P_4S_3 ; (3) a slightly positive reaction with safety match tip (contains antimony sulphide Sb_2S_3 , and an oxidizing substance); (4) slightly positive patch test with striking surface of safety box (contains red phosphorus and an oxidizing agent). The patch tests with 10% sulphur ointment were negative in each case.

That this process is partially one of contact with the fumes of burning match tips is shown by this observation. Case 2, for one day used several friction matches to light cigarettes and in twenty-four hours developed itching and a moderate dermatitis about the eyes. At a later date, when this had entirely subsided, she was asked to particularly handle the tips of friction matches for one day. In eight hours, she had developed a much more severe dermatitis about the eyes from the contact of the fingers with her eyes due to a greater concentration of the offending material. Case 1 handled the match tips for one day, but carefully kept her fingers from her eyes and no dermatitis resulted.

The tip of a friction match is made up of an igniting portion which contains phosphorus sesquisulphide together with substances which are

also present in the burning portion, namely an oxidizing agent such as potassium chlorate with combustible substances such as sulphur, paraffin, glue, and abrasives. A safety match is dipped in a readily combustible substance such as antimony sulphide Sb_2S_3 and an oxidizing agent such as potassium chlorate, whereas the striking side of the box contains red phosphorus and an oxidizing agent together with abrasives and glue.²

Yellow phosphorus is semi-transparent, soft and waxy, has a garlic-like odour, and is poisonous. Its use in making matches was long ago discontinued because the match factory workers developed "phossy-jaw". Red phosphorus is made from yellow phosphorus by its exposure to high temperatures in a vacuum, is more stable, oxidizes much less rapidly, and is non-poisonous. This allotropic variant is now used in the manufacture of matches in the form of phosphorus sesquisulphide P_4S_3 . "When heated, red phosphorus sublimes forming vapour composed of molecules of P_4 . Upon condensation of the vapour, the yellow form is produced."²

As an industrial hazard, apart from acute phosphorus poisoning, phosphorus absorption from fumes over a long period of time (two to five years) may result in loosening of the teeth from variable degrees of necrosis of the jaw and caries of the teeth. It is said that necrosis results in and about carious teeth, the presence of bacteria being necessary. Workers who handle phosphorus frequently develop burns and caustic lesions, dermatitis, conjunctivitis, itching, or nasal irritation. Chronic symptoms include a garlic odour, increased red and white cell count, enlarged liver followed later by jaundice, anaemia, and jaw necrosis with general prostration. (This refers to yellow phosphorus³).

These cases of dermatitis about the eyes and face due to contact with and hypersensitivity to the fumes of match tips and associated with loosening of the teeth and dental caries, have not been recognized and may be not uncommon. The duration in both cases was long. While direct contact with match ends may produce an acute dermatitis about the eyes when carried by finger tips, it is neither customary nor common that in the handling of such matches for lighting purposes the inflammable tip of the match is touched. Individuals for practical purposes only contact the wooden end; particularly is this true of females, who do not carry friction matches as a rule.

The cutaneous manifestations may be explained by a sensitivity to phosphorus sesquisulphide and its combustion products. On the other hand, the causes of the toxic manifestations, notably present in Case 1 and the dental changes in both cases, be they of similar origin, are somewhat more difficult to assess. It is possible that unoxidized atoms of phosphorus may be present in match combustion vapour but it would seem unlikely. Incomplete oxidation forms of phosphorus, the best known of which are the trioxide P_4O_6 and the pentoxide P_4O_{10} , or of the phosphorus sulphides, could, through inhalation, give rise to slower but similar phenomena as those seen in factory workers when exposed to yellow phosphorus.

SUMMARY

Two cases of poisoning in females by the fumes of burning match tips (containing phosphorus sesquisulphide) arising over a long period of time through the daily lighting of friction matches are described. This poisoning resulted in a recurring severe primary dermatitis about the eyes and face. In each case, loosening of the teeth occurred which may have been due to phosphorus poisoning. In one case a severe systemic poisoning resulted which cleared up completely on discontinuing the use of matches. The possible means by which this systemic and cutaneous poisoning could have resulted are discussed.

REFERENCES

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2. BRISCOE, H. T.: General Chemistry for Colleges (4th ed.), Houghton Mifflin Co. (Riverside Press) Cambridge.
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RÉSUMÉ

L'auteur cite deux cas d'empoisonnements par le sesquisulfure de phosphore qui sont survenus chez des femmes, au cours d'une longue période de temps et à la suite de l'allumage quotidien d'allumettes ordinaires à friction; cet empoisonnement tenait aux vapeurs provenant de la combustion des bouts d'allumette enduits de phosphore.

L'intoxication exogène prit la forme d'une dermatite primitive grave située à la face et au pourtour des yeux et elle fut accompagnée dans chaque cas par un décollement marqué des dents, qui était probablement causé par une nécrose de la mâchoire directement imputable à l'inhalation des vapeurs. Dans un de ces cas, une septicémie grave fit suite à l'apparition de ces autres symptômes.

Il semble bien qu'il faille trouver l'explication de ces phénomènes dans la conversion du phosphore rouge non toxique dans les bouts d'allumettes en un phosphore jaune toxique, changement qui s'opère au cours de la combustion.