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Reaction of chrysotile asbestos with triphenylmethane dyes

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Triphenylmethane dyes react at ambient conditions with chrysotile asbestos to form homogeneously coloured fibres. Formation of the chelates on the fibre varies: for Basic Fuchsin, Malachite Green and Methyl Blue equilibrium is reached in 1 h, the concentration on the fibre is 1% to 2.4%, and increases slightly on boiling. For Brilliant Blue R, Crystal Violet, and Methyl Violet equilibrium is reached after 16 to 24 h, the concentration on the fibre is 8% to 10%, and increases greatly on boiling reaching 10% to 31%. No precipitates were observed on the coloured fibre under the scanning electron microscope indicating a chelate formation. This was also supported by X-ray diffraction and infrared analysis.

1. Introduction

Dyestuffs have been used for many decades to stain cells and microorganisms for identification purposes [1]. They have also been used to identify clay minerals through a colour reaction, e.g. montmorillonite gives a blue colour with benzidine but illite does not [2]. Reactions like these were exploited by engineers to separate minerals by flotation [3]. For example, Alizarine Red S is more adsorbed on apatite than calcite, hence separation by flotation can be made possible [4]. Fly ash, which is mainly a silicate, is suggested as a cheap material for removal of certain dyestuffs from textile waste water [5]. Activated charcoal is also used for the same purpose. Dyestuffs are also adsorbed on metallic surfaces to inhibit their corrosion [6] and used to colour certain metals on which an anodic oxide film has formed [7]. This shows the diversified reactions of dyestuffs with materials other than textile fibres – their most important application.

In the present investigation the reaction of dyestuffs with chrysotile asbestos was studied to find out more about their behaviour on such an industrial mineral of great economic importance, particularly when little information is available on this subject [8]. Chrysotile asbestos has the advantage of a large surface area and, unlike activated charcoal, is white in colour so that the action of dyes can be followed easily. Valerio *et al.* [9] used Acridine Orange, Methylene Blue (thiazine structure), Eosine Y (structure related to phthaleins), and picric acid in their adsorption studies on asbestos. They found that the first two, which are basic dyes, were sorbed, while the last two, which are acid dyes, were not sorbed. In the present study, basic dyes with triphenylmethane structure were selected for initial investigation; it is intended to study other types of dye in the future to elucidate the mechanism of adsorption.

2. Experimental details

2.1. Materials

Asbestos sample 7RF-66 originated from the Province of Quebec and was supplied by the Asbestos Institute of Montreal. This sample has a short fibre and its chemical analysis is shown in Table I. Dyes used from the triphenylmethane group were: Basic Fuchsin, Brilliant Blue R, Crystal Violet, Malachite Green, Methyl Blue, and Methyl Violet. Phenolphthalein and Bromocresol Purple, although not dyes, were used as representative members of the phthalein group with triphenylmethane structure. A description of these compounds as well as their formulae is given in Table II and Fig. 1.

2.2. Procedure

An asbestos sample of 1 g was agitated for 1 h at room temperature with 100 ml solution containing variable amounts of the dyes under study using a magnetic stirrer. The suspension was filtered and analysed to determine the amount of dye sorbed by the fibre. The filter cake was washed thoroughly with water to remove all soluble components, dried at 80° C, then examined under the optical and scanning microscope. Some tests were conducted at boiling point; it was found necessary to study the thermal stability of the dyes themselves. In other tests, 1 g $Mg(OH)_2$ (Fisher)

TABLE I Analysis of chrysotile asbestos CCM Grade 7 RF-66

	%		%
SiO_2	35.24	S	0.027
MgO	42.94	Cu	0.0
Al_2O_3	0.04	Ni	0.19
CaO	0.13	FeO	1.31
CrO_3	0.20	Fe_2O_3	4.33
MnO	0.05	Loss on ignition	14.42
CO_2	0.91		
		Total	99.79

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TABLE II Triphenylmethane dyes

Dye	Colour Index	Formula Weight	λ_{max} (nm)	Dye content (%)	Supplier
Basic Fuchsin (Basic Violet 14, Rosaniline)	42 510	337.86	540	100	Poly Inc. Pennsylvania
Brilliant Blue R (Acid Blue 83)	42 660	825.99	585	≃ 70	Sigma
Bromocresol Purple*		540.24	419	100	DIFCO
Crystal Violet (Basic Violet 3)	42 555	407.99	588	93	DIFCO
Malachite Green	42 000	328.48	618	100	BDH
Methyl Blue (Aniline Blue)	42 780	799.82	600	100	BDH
Methyl Violet (Basic Violet 1)	42 535	393.96	584	85	Aldrich
Phenolphthalein*		318.33	557	95	Fisher

*Not a dye.

was agitated with 100 ml solution of some of these dyes ($1\,g\,l^{-1}$) at room temperature. The coloured product was separated by filtration and analysed by X-ray diffraction and infrared spectroscopy to be compared with asbestos fibre coloured with the same dyes.

2.3. Analytical determinations

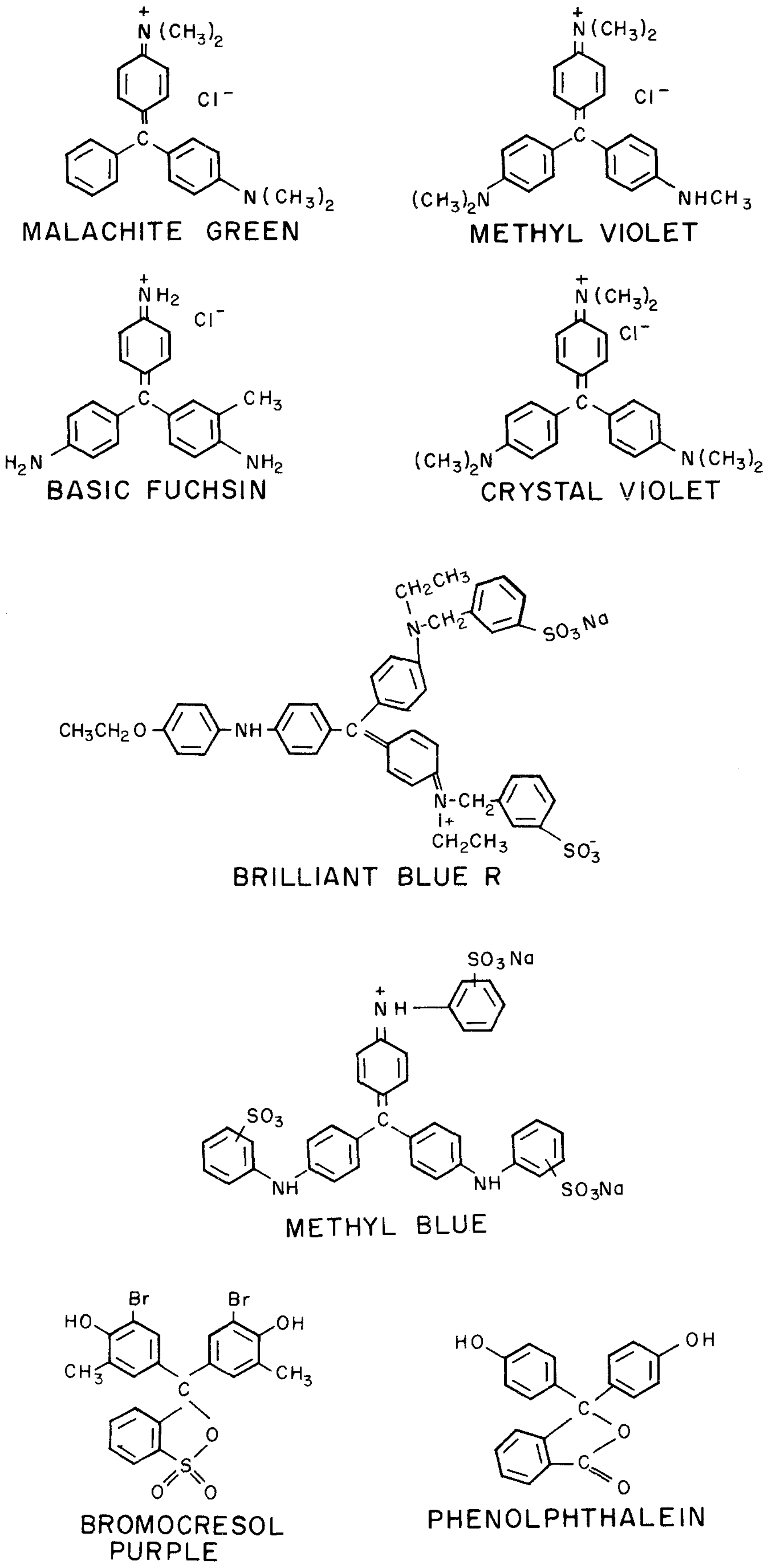
The amount of dye sorbed by the fibre was calculated from the concentrations before and after contact. The concentrations were determined spectrophotometrically at the maximum absorption of the reagent in solution. Standard curves were prepared by dissolving a certain amount of the reagent in water to make a stock solution from which other solutions of known concentrations were obtained by dilution.

Because Mg^{2+} is known to be released when asbestos is in contact with aqueous solution, it may be complexed by the dye. Therefore all standard curves were prepared from solutions containing an excess of Mg^{2+} ions. It was established that when the concentration of Mg^{2+} ions was 10 to 20 times that of the stoichiometric concentration of the dye, the absorbance was constant and reproduceable. The ultraviolet spectra of the dyes used in the absence and presence of excess Mg^{2+} ions (250 and 500 times) were made from which the wavelength at maximum absorbance was determined. All solutions of the dye containing Mg^{2+} were clear; turbidity and precipitates formed only when excessive Mg^{2+} ions were present. There was no shift in the peak due to Mg^{2+} ions. In the case of Methyl Blue, the remaining solution after sorbtion of the dye becomes colourless due to its alkaline pH; to determine the concentration of the dye in such a solution it was necessary to restore the colour by acidification. In case of Malachite Green it was not possible to determine the concentration of residual dye because it decomposed on standing and on boiling (and cannot

TABLE III Colour of triphenylmethane dye solutions and chelates formed on chrysotile asbestos

	pH of application	Colour of dye solution	Colour of chelate
Basic Fuchsin	9.5–10	Purple	Colourless
	5–6	Red rose	Pale red
	2–3	Pale red	Pale red
Brilliant Blue R	9.5–10	Colourless	Blue
	6–7	Blue	Blue
	2–3	Blue	Blue
Bromocresol Purple*	9.5–10	Violet	Blue
	6–7	Yellow	Yellow
	2–3	Yellow	Yellow
Crystal Violet	9.5–10	Violet	Violet
	5–6	Violet	Violet
	2–3	Greenish yellow	Greenish yellow
Malachite Green	9.5–10	Greenish blue	Pale blue
	6–7	Greenish blue	Pale blue
	2–3	Green	Greenish blue
Methyl Blue	9.5–10	Colourless	Blue
	6–7	Blue	Blue
	3–5	Blue	Blue
Methyl Violet	9.5–10	Violet	Violet
	6–7	Violet	Violet
	1–3	Greenish yellow	Greenish yellow
Phenolphthalein*	9.5–10	Pink	Pink
	6–7	Colourless	Pale pink
	2–3	Colourless	Colourless

*Not a dye.



MALACHITE GREEN

METHYL VIOLET

BASIC FUCHSIN

CRYSTAL VIOLET

BRILLIANT BLUE R

METHYL BLUE

BROMOCRESOL PURPLE

PHENOLPHTHALEIN

Figure 1 Structural formulae of triphenylmethane dyes used.

be restored by acidification) as will be explained later.

The standard curves for the dyes used in the presence of Mg^{2+} ions were all linear at the concentrations used (2 to 20 p.p.m.). Because some dyes were not 100% pure (see Table II), this was taken into consideration when preparing these curves.

2.4. Equipment

A Hewlett Packard Model 8450A UV/VIS Spectrophotometer connected to a Model 82901M flexible disc drive was used. X-ray diffraction was carried out with a Philips PW1011 Generator, PW1050 goniometer, and infrared spectrophotometry with a Beckman

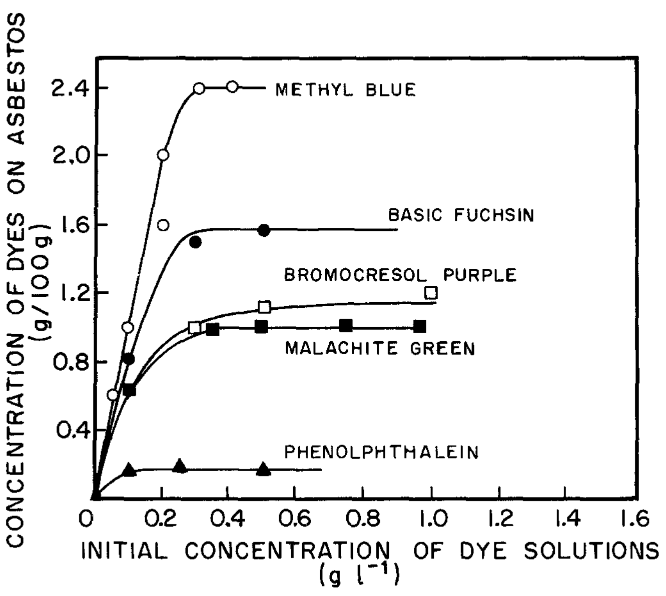


Figure 2 Equilibrium concentration for some triphenylmethane dyes with asbestos.

Model IR 4200 – series. The pH meter was a Corning, Model 5, and the scanning electron microscope was a Joel JSM-25S III.

3. Results and discussion

When the dyes were dissolved in water they gave coloured basic solutions, except Methyl Violet and Brilliant Blue R which were colourless (Table III). Basic Fuchsin was partially soluble in water; complete solubility was obtained by acidification. However, a colour change usually took place when Mg^{2+} ions were added: colourless Methyl Blue became blue while Basic Fuchsin became colourless. The colour change was also a function of pH; for example, Bromocresol Purple at pH 9.5 to 10 is violet, while at pH 2 to 7 it turns yellow; the colour of the chelate with Mg^{2+} ions or asbestos is also a function of the pH.

3.1. The chelation process

Asbestos fibres treated with the dyes were vividly coloured and the colour was stable on boiling with distilled water under a reflux condenser for 1 h, thus indicating that the dye is chemically bound to the surface of asbestos. Coloured asbestos, when thoroughly washed and dried then slurried with water, has the same pH as the original uncoloured sample. Under the microscope the coloured samples were fully homogeneous and no precipitates were visible.

X-ray diffraction study of the coloured products revealed the following points.

1. New peaks appeared for asbestos chelated with Crystal Violet and Brilliant Blue R, while no change took place for $Mg(OH)_2$ chelated with the same dyes.
2. No peaks appeared for asbestos chelated with Methyl Violet while a new peak appeared in the case of $Mg(OH)_2$ chelated with the same dye.

On the other hand, infrared study of the coloured products revealed new peaks for asbestos chelated with Crystal Violet, Methyl Violet, and Brilliant Blue R in the region (1150 to 1650 cm^{-2}). These peaks coincide with those appearing in the same region for $Mg(OH)_2$ chelated with the same dyes. No change in the infrared or X-ray patterns for products coloured with Malachite Green, Basic Fuchsin, Methyl Blue, Bromocresol Purple, and Phenolphtalein was seen, probably because their concentration on the fibres was low.

The appearance of new peaks in X-ray diffraction patterns and in infrared spectra together with the absence of precipitates as revealed by scanning electron microscopy, supports the view that chelates are formed with asbestos, apparently with its $Mg(OH)_2$

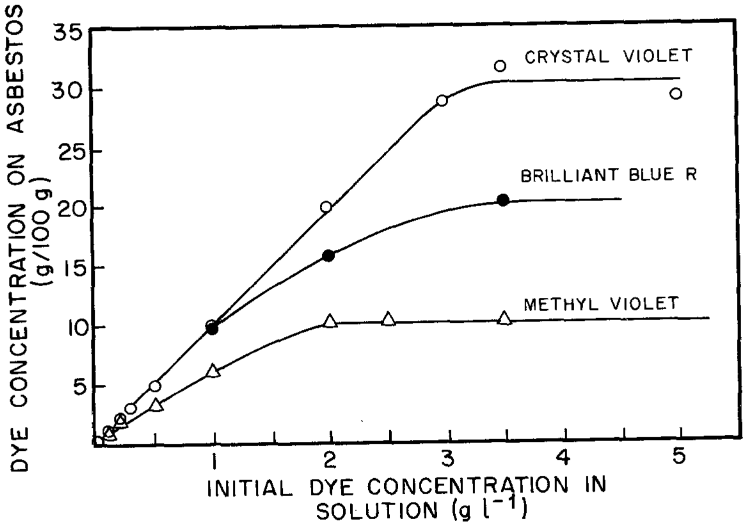


Figure 3 Dyeing asbestos with Crystal Violet, Brilliant Blue R, and Methyl Violet at the boiling point.

TABLE IV Maximum sorbtion of triphenylmethane dyes on chrysotile asbestos at various temperatures, one hour agitation

Chelating Agent	Maximum loading (%)	
	25° C	100° C
Basic Fuchsin	1.6	1.9
Brilliant Blue R	6.5	20.0
Bromocresol Purple	1.0	1.2
Crystal Violet	1.0	31.7
Malachite Green*	1.0	*
Methyl Blue	2.4	2.5
Methyl Violet	0.8	10.0
Phenolphthalein	0.2	0.3

*Colour disappears on boiling

component. This resembles the process of mordant dyeing of textile fibres where $Mg(OH)_2$, $Al(OH)_3$ or $Cr(OH)_3$ are first precipitated on textile fibres then contacted with the dye solution to form what was known as "lakes" [10].

Fig. 2 shows the maximum concentration of dyes on asbestos at equilibrium resulted by contacting 1 g asbestos with dyes at different concentrations in 100 ml dye solution for 1 h; it reached 2.4% for Methyl Blue, while for Phenolphthalein it did not exceed 0.2%.

3.2. Effect of boiling

When asbestos was boiled with the dye solutions, increased amounts of dye were sorbed in the case of Crystal Violet, Brilliant Blue R, and Methyl Violet; the concentrations were 31%, 20% and 10%, respectively. For other dyes there was slight change (Table IV and Fig. 3). Scanning photomicrographs showed no precipitate formation on the fibre. To ensure that the analytical determinations were not subject to an error due to boiling, the thermal stability of aqueous solutions of the dyes in the presence and absence of Mg^{2+} ions was studied by ultraviolet spectroscopy. It was found that the dye solutions were stable on boiling whether Mg^{2+} ions were present or not, except those of Methyl Blue and Malachite Green in the presence of Mg^{2+} ions, the colour disappeared. In the case of Methyl Blue, the colour was restored by acidification while in the case of Malachite Green the colour could not be restored; in this case it was not possible to determine its concentration on asbestos on boiling.

3.3. Effect of time

The effect of time on dyeing is shown in Fig. 4. It was found that in some cases the reaction was complete in 0.5 h, while in others, e.g. Crystal Violet, Methyl Violet, and Brilliant Blue R, it took about 24 h for completion. In the case of Malachite Green, the colour intensity decreased with time; it was thus not possible to determine the amount of the dye sorbed after 1 h.

3.4. Chelation and structure

No correlation could be found between the structure of the dye and the quantity sorbed on the fibre. For example:

1. While Basic Fuchsin, Malachite Green, Crystal Violet, and Methyl Violet have nearly the same structure and the same formula weight, the first two behave in a markedly different manner from the last two. Thus Basic Fuchsin and Malachite Green are sorbed rapidly, their maximum concentration on the fibre is 1.6% and 1.0%, respectively, and did not increase significantly on boiling. On the other hand, Crystal Violet and Methyl Violet are sorbed slowly, their maximum concentration on the fibre is 10% and 8%, respectively, and increased to 30% and 10% on boiling.

2. Brilliant Blue R and Methyl Blue have nearly similar structure and formula weight but behave differently. The first is slowly sorbed and reaches a high concentration on the fibre (about 20%) while the second is rapidly sorbed and reaches only 2.4% on the fibre.

Although Bromocresol Purple and Phenolphthalein are not dyestuffs, they colour asbestos. They have nearly similar structure and behave nearly the same towards asbestos.

4. Conclusions

1. Chrysotile asbestos can be dyed with triphenylmethane dyes at ambient conditions and the process

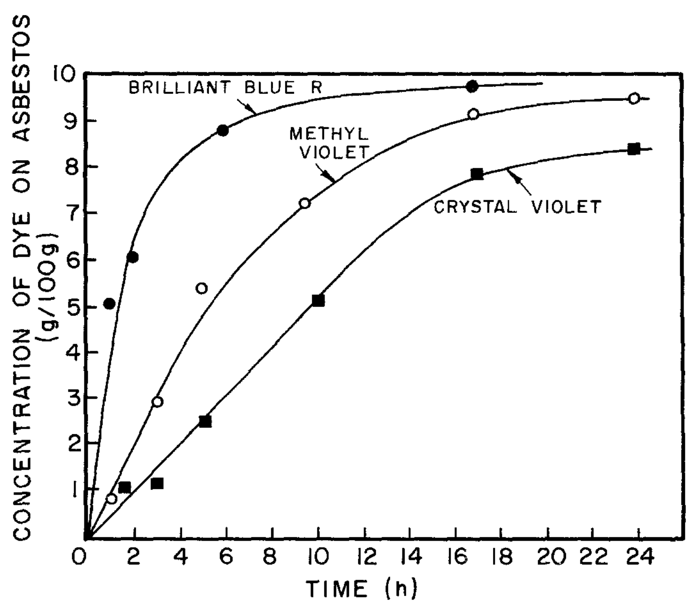


Figure 4 Effect of time on dyeing asbestos with Brilliant Blue R, Methyl Violet, and Crystal Violet.

seems to be a chelate formation with the $Mg(OH)_2$ component of asbestos. In this way the dyeing process is similar to mordant dyeing on textile fibres. Chelation is supported by the appearance of new peaks in X-ray diffraction analysis and infrared spectroscopy of the coloured products, while scanning electron microscopy showed no precipitates.

2. The reaction is fast with Basic Fuchsin, Malachite Green, and Methyl Blue, equilibrium is reached in less than 1 h. The amount of dye sorbed by the fibre is 1% to 2.4% and increases slightly on boiling. For Brilliant Blue R, Crystal Violet, and Methyl Violet the reaction is slow; equilibrium is reached in 16 to 24 h. The amount of dye sorbed by the fibre is 8% to 10% and increases on boiling to 10% to 31%.

3. Bromocresol Purple and Phenolphthalein colour asbestos although they are not dyes, apparently due to formation of chelates.

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