

## NOTES AND NEWS

### DARKENING OF CINNABAR IN SUNLIGHT

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During the course of an investigation of cinnabar ores, it was found that some specimens show the peculiar tendency to turn superficially black, relatively rapidly, on exposure to sunlight. Insofar as the writer is aware, this rapid darkening is shown by cinnabar from only the following four localities: (1) the Opalite mine and associated deposits located in southeastern Oregon, a few miles north of the town of McDermitt on the northwestern Nevada-Oregon border; (2) the Goldbanks deposit located about thirty five miles south of Winnemucca, Nevada; (3) some of the cinnabar in siliceous sinter at Steamboat Springs, Nevada; and (4) ore from the B and B mine in Esmeralda County, Nevada. The darkening of cinnabar at the third locality is known to the writer only through conversation with Professor V. P. Gianella and that at the fourth locality, through information received from Dr. R. W. Webb. At all four of these localities the cinnabar occurs disseminated through hydrothermal silica formed at or near the surface. At least in the Goldbanks deposit, the cinnabar and silica have been deposited syngenetically and the admixture is so intimate that it is impossible to effect a complete separation of cinnabar from silica. Ransome<sup>1</sup> has stated that all cinnabar darkens on exposure to sunlight. Upon exposure for a long period, this may be true, since it likewise has been noted that cinnabar vermilion used in painting darkens after a number of years.<sup>2</sup> However, within a period of a few months, or a somewhat longer period, this darkening is not characteristic of all cinnabar since the writer has seen a number of museum specimens and open pit exposures which are still bright red after exposure to sunlight for several years. A specimen of cinnabar from the Aurora mine in San Benito County, California, as well as cinnabar concentrated from a specimen collected by Ransome in the Mazatzal Mountains of Arizona were exposed to sunlight for six months without any change being noted.

Table 1 tabulates the results of experiments on natural and artificial red mercuric sulphide.

A specimen of the low grade Opalite ore was mounted in bakelite and polished. The section was then exposed to sunlight in air and the decrease

<sup>1</sup> Ransome, F. L., *Quicksilver: U. S. Geol. Survey, Mineral Resources* 1917, pt. 1, 392 (1921).

<sup>2</sup> Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 4, 951.

TABLE 1. EXPERIMENTS ON THE DARKENING OF RED MERCURIC SULPHIDE IN SUNLIGHT

Sample	In air	In water	In 10% KOH	In darkness
Mercuric sulphide prepared by sublimation	Not darkened in 10 weeks	Not darkened in 10 weeks	Not darkened in 10 weeks	
Mercuric sulphide prepared by wet method	Not darkened in 10 weeks	Not darkened in 10 weeks	Not darkened in 10 weeks	
$\beta$ -HgS	Not darkened in 8 weeks	Not darkened in 10 weeks	Darkened in 8 days	Not darkened in 10 weeks in 10% KOH or in 1 year in air
Cinnabar ore from Aurora mine	Not darkened in 8 months	Not darkened in 10 weeks		
Concentrates of cinnabar ore from Mazatzal Mts.	Not darkened in 8 months	Not darkened in 10 weeks	Darkened in 2 weeks	
Low grade Goldbanks ore	Darkened in Winnemucca and Washington in 5 days Darkened in Pasadena in 8 weeks	Not darkened in 10 weeks in Pasadena	Darkened in 8 weeks in Pasadena	Not darkened in 5 months
High grade Goldbanks ore	Not darkened in 10 weeks in Pasadena, nor in 2 weeks in Winnemucca	Not darkened in 10 weeks in Pasadena	Not darkened in 8 weeks in Pasadena	Not darkened in 5 months
Low grade Opalite ore	Darkened in 2 days	Darkened in 2 days	Darkened in $\frac{1}{2}$ hour	Not darkened in 6 months in air, but darkened in $\frac{1}{2}$ hour in KOH
High grade Opalite ore	Darkened in 4 weeks	Not darkened in 10 weeks	Darkened in 2 days	Not darkened in 6 months in air nor in 2 weeks in KOH

in internal reflection noted every three hours. The internal reflection decreased gradually until none remained after two days. Since the cinnabar itself is dispersed through silica, the character of the darkened compound could not be determined from the polished section.

The experimentally determined relationships are rather confusing, but can be summarized as follows:

(1) Cinnabar in low grade ore darkens on exposure to sunlight more rapidly than that in high grade ore.

(2) When the darkening occurs, alkali seems to accelerate the rate of darkening.

(3) Water appears to decrease slightly the rate of darkening.

(4) The rate of darkening varies greatly for mercuric sulphide prepared in various ways.

(5) All known naturally occurring cinnabar that darkens rapidly occurs in a matrix of hydrothermal silica.

The darkening under discussion involves a change in the color from red to black of a very thin surficial layer of cinnabar. Longer exposures, as noted at the Goldbanks mine, intensifies the darkening, but does not increase the thickness of darkened layer. Heumann<sup>3</sup> states that acids inhibit the darkening; that under pure water the change is very slow; but that under alkaline conditions the darkening occurs in a few minutes, and that cinnabar prepared by the wet method darkens more rapidly than that prepared by sublimation. The writer has been unable to duplicate Heumann's results. Allen and Crenshaw<sup>4</sup> observed that, when cinnabar is heated to 325°, the surface turns black, but that the red color returns when the cinnabar is cooled. If the cinnabar is heated to 445° the darkening is permanent. The surficial change in the color of cinnabar from red to black in sunlight often has been assumed to be a change from cinnabar to metacinnabar. However, the fact that the same surficial darkening is observed when cinnabar is heated (although metacinnabar is a monotropic form which, at high temperatures, is converted to cinnabar) casts doubt on the validity of this assumption. Dr. Schaller<sup>5</sup> has reminded the writer that some metals such as platinum, when precipitated in a very finely divided state, are black. The writer prepared a solution of colloidal mercury by dilution of an alkaline mercuric sulphide complex solution. When this solution is poured over a porcelain surface, a mercury mirror is deposited. When the mercury mirror is wiped off with a cloth the deposit on the cloth is black. There is, therefore, no reason why

<sup>3</sup> Heumann, Karl, Veränderung den Zinnober durch das Licht: *Ber. deut. chem. Gesell.*, **7**, 750-51 (1874).

<sup>4</sup> Allen, E. T., and Crenshaw, J. L., *Am. Jour. Sci.*, 4th series, **34**, 379 (1912).

<sup>5</sup> Schaller, W. T., Personal communication.

the darkening of cinnabar could not be the result of the formation of a surficial layer of colloidal mercury in solid solution in the cinnabar. The darkened layer is not removed by nitric acid as it should be were it mercury. However, silver halides, covered with a solution of nitric acid in which metallic silver is soluble, darken on exposure to sunlight. The current theory explaining the darkening of silver halides, therefore, likewise postulates a surficial dispersion of silver as a solid solution in the silver halide<sup>6</sup> since metallic silver in solid solution would not be removed by nitric acid. Despite the long use of photographic emulsions, the exact cause and character of the darkening of silver halides is still not known definitely. One of the difficulties in studying photosynthetic compounds is due not only to the small amount of the synthesized substance which is formed, but also to the fact that very small differences in the medium in which the compound is imbedded cause a wide variation in the photosensitivity of the compound. Although it has long been known that variations in the emulsion cause a great variation in the sensitivity of silver halides to light, the fact was only recently discovered that the sensitivity of the halides is greatly increased by the presence in the emulsion of minute amounts (1:300,000 to 1:1,000,000) of allyl isothiocyanate (C<sub>3</sub>H<sub>5</sub>CNS—allyl mustard oil).<sup>7</sup> By analogy, it is possible that some minute impurity in the cinnabar or adjacent wall rock might greatly affect the photosensitivity of the cinnabar and explain some of the observed anomalies.

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<sup>6</sup> Mellor, J. W., *op. cit.*, 3, 414.

<sup>7</sup> Wall, E. J., *Photographic Emulsions*, 25-7 (1929).

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