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COLORING MATTER IN THE CALIFORNIA RED WINES.[1]

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DURING the last three quarters of a century the coloring matter of red wines has been carefully investigated. Those undertaking the work have endeavored to find some reaction or series of reactions, by which the natural coloring matter of the grape could be distinguished from that of other fruit and vegetables with which wines are so frequently adulterated. The introduction of the aniline colors into this industry attracted for a time a portion of the attention which had previously been given entirely to the vegetable colors, and methods have been brought forward by which the former can be recognized. On account of the comparative ease and certainty with which the aniline colors con be detected, wine makers still give their preference to the vegetable pigments, and a method for their detection is still regarded as desirable. A large number of methods have been suggested for this purpose, but most of them have proved worthless, and none of them at all satisfactory.

Among the difficulties which have been encountered by workers in this field, and which have not yet been overcome, are the following:

1. Many of the substances employed for coloring wines are so nearly identical with the natural coloring matter of the grape that it would not be an easy matter to distinguish between them even in freshly prepared solutions.

2. The coloring matter of wine changes materially with age, and different reactions are given by samples of the same variety and from the same locality, but of different vintages.

3. Different reactions are commonly obtained with wi[illegible] the same age, but of different varieties or from different parts of the country.

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[1] Read before the Washington Section in abstract, November 8, 1894, and before the American Chemical Society, December 27, 1894.

As an example of the difficulties which are met with in making use of any of the methods that have been brought forward, let us notice the action of lead subacetate. According to Vögel this reagent gives a grayish green precipitate with pure wines, while with wines colored with elderberries, the juice of beets, &c., a precipitate colored indigo-blue, red, or some equally characteristic color is obtained. A more careful examination of the method revealed the fact that a number of fortified wines known to be free from foreign coloring matter gave distinct red and violet precipitates, while elderberries and mallow added to some of the lighter wines could not be detected. The same difficulties are experienced to a greater or less extent in all methods which have been suggested, and it is now customary in examining a wine for foreign vegetable coloring matter, to compare it with a wine of known purity, of the same variety, the same vintage, and from the same locality, as the sample under examination.

This work with California wines was done under the direction of Dr. H. W. Wiley, and was in connection with the examination made during the past year of the samples furnished by the California Viticultural Association. In all, ninety-four samples of California red wines were examined. Their age varied from one to seven years.

No wines were available which were known to be colored with vegetable pigments, and the facilities for coloring them were lacking, since wines colored after fermentation are quite different from those fermented after the addition of colored vegetable material to the must. This work was not undertaken, therefore, with the hope of developing a method for the detection of foreign coloring matter in wine, but merely for the purpose of studying the coloring matter of California wines, and of recording the reactions given by some of the reagents, whose reactions with the European wines have been the subject of so much careful study. The number of reagents employed was limited by the size of the samples.

For convenience the methods which were employed are divided into three classes. The methods given in the first class give a red, blue, or violet color with wines containing foreign coloring matter, and usually a green or grayish green tint when the wines are pure.

The second class of reagents includes certain metallic oxides, such as manganese dioxide and lead dioxide. These have been used in different proportions, sometimes to distinguish between natural wines and those colored with foreign vegetable colors, sometimes between the vegetable colors and coal-tar colors in wine. They have not been found entirely satisfactory, since the amount necessary to decolorize some pure wines is sufficient to destroy even the aniline colors in some that had been artificially colored. Yet they have been found of great assistance in the examination of such wines as claret and burgundy. These reagents were found to destroy almost all the color in California wines when used in the proportions recommended for French claret and similar wines.

The third class includes methods which use chalk treated with albumen and charged with varions reagents.

CLASS I.

Lead Acetate—Neutral and Basic.—The reactions obtained with neutral and basic lead acetate were almost identical. The precipitates were yellowish green, grayish green, gray or brown. No blue, red, or violet colors were obtained.

Sodium Carbonate.—In the use of this reagent the solution recommended by Gautier (Sophistication et analyse des vins, 4me. edition, page 211) was employed. One cc. of wine was mixed with five cc. of a five-tenths per cent. solution of sodium carbonate. The colors obtained were brown, yellowish brown, and yellowish to grayish green.

Sodium Bicarbonate.—Gautier's solution was also employed with this reagent. Eight grams of sodium bicarbonate were dissolved in 100 cc. of water and the solution saturated with carbon dioxide. Equal volumes of this solution and the wine under examination were mixed and the color noted. The reactions obtained were gray or grayish green, with sometimes a tinge of brown.

Ammonia.—The action of dilute ammonia on red wine was first pointed out by Chevallier in 1827, and since then it has been commonly used in their examination. The solution used in this work contained one part of strong ammonia to nine parts of water. This was then added to wine in equal volumes, and the resulting mixture was filtered when turbid. The filtrates were colored various shades of brown and green with an occasional orange-red.

Ammonium Hydroxide and Ammonium Sulphhydroxide.—A mixture of twenty cc. of ammonium hydroxide and eight cc. of ammonium sulphhydroxide were diluted with water to one liter, and a portion of five cc. treated with an equal volume of wine. The resulting solutions were brown to yellowish brown.

Alum and Potassium Carbonate.—Five cc. of a saturated solution of ammonia alum were mixed with ten cc. of wine, five cc. of a one-tenth solution of potassium carbonate added, and the whole stirred and filtered. The precipitates were gray or yellowish brown with sometimes a tinge of green. The filtrates were sometimes of a light wine color, but were not lilac or wine-colored in any case.

Alum and Lead Acetate.—This method is the same as the preceding except that a one-tenth solution of lead acetate is used instead of potassium carbonate. The precipitates were colored yellowish gray to brown except in three cases, when they were of a light wine color.

Borax.—Two volumes of a saturated solution of borax were mixed with one of wine. A brown to yellowish brown color was obtained with all wines except one sample of Gutedel, which gave an orange-red color.

Copper Sulphate.—Ten cc. of wine were diluted with water to 100 cc. and thirty cc. of a saturated solution of copper sulphate added. The color of the solution was changed in every case to a light olive-green.

Tartar Emetic.—Two to three volumes of wine were mixed with one volume of a saturated solution of tartar emetic. The color was changed in every case to a bright cherry-red.

CLASS 2.

Manganese Dioxide.—100 cc. of wine were shaken for fifteen minutes with fifteen grams of manganese dioxide, and the mixture filtered. The filtrates were light colored, but were not entirely decolorized in any case. Shaking the filtrates with another portion of fifteen grams of maganese dioxide rendered them almost colorless.

Lead Peroxide.—Five grams of lead peroxide were added to twenty cc. of wine, and the mixture well shaken and filtered. Some of the filtrates were entirely decolorized, though in many of them a very light wine color remained.

Mercuric Oxide.—Ten cc. of wine were shaken for one minute with three-tenths to four-tenths gram precipitated mercuric oxide (Cazeneuve uses one to one and one-half grams) and filtered. The filtrates were all colorless or light yellow.

CLASS 3.

Sodium Peroxide.—M. Ruisand uses sodium peroxide to detect aniline coloring matters in wine. He adds ten to fifteen cc. of sodium peroxide to five cc. of wine, allows it to stand twenty minutes, and renders slightly acid with acetic acid. According to Ruisand, both vegetable colors and aniline derivatives are decolorized by the peroxide, while the coal-tar colors are restored by acetic acid.

With the California wines the color is not entirely destroyed, even with twice the quantity of peroxide recommended by Ruisand, and in many cases a marked wine color remained both before and after acidification.

A lump of chalk was cut into pieces about fifteen mm. square and half as thick, and one side of each piece was carefully smoothed with a knife. These pieces of chalk were then immersed for two hours in a ten per cent. solution of egg albumen and dried at 45°. They were then divided into five portions, one of which was reserved for testing the wine without further treatment, and each of the other four immersed for forty minutes in a one per cent. solution of one of the following reagents: Tartar emetic, lead acetate, copper acetate, and zinc acetate. After being dried at 50°, they are ready for use. Three drops of each wine examined were placed on the smooth surface of one block from each of the five divisions given above, the blocks dried at 100° for one hour, and the color noted. Another block from each division was treated with the same amount of wine, dried for twenty-four hours at the temperature of the laboratory, and the color compared with that of the blocks dried at 100°. The colors obtained were brown, grayish brown, and slate colored. No tinge of violet, blue, or green, was obtained in any case. In every case the color of the block dried at 100° was almost, if not exactly, identical with that of the block treated with the same wine and dried at the temperature of the laboratory.

According to the reactions obtained with these reagents, the coloring matter of California wines appears to be much more uniform than that of European wines. The reactions are not always the same as those obtained with the more ordinary European wines; for instance, a gray, or yellowish, or orange-gray precipitate or solution is sometimes obtained with reagents which are said to give green or grayish green with French wines. On the other hand no reactions were obtained which are said to be characteristic of wines colored with vegetable pigments.

THE PENETRATION MACHINE—AN EXPLANATION.

By H. C. Bowen.

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On page 59, January number, 1895, of this Journal, a somewhat vague reference is made to a testing instrument. The identity of the instrument referred to is made manifest to me by the context. The instrument is known by those who have to do with it as the Penetration Machine; first described in print by myself in the School of Mines Quarterly, **10**, 297, under the title "An Apparatus for Determining the Relative Degree of Cohesion of a Semi-Liquid Body." The reference above noted, by some mischance, does the instrument and its work injustice. The origin of the instrument was due to pressing needs in the technology of alsphalt cements used for paving purposes. These cements, made by different parties using different tempering agents, were very varied, and at the time of the origin of this instrument there was no way other than chewing the cement for foremen to test whether the cement was of required consistency or not. Since that time (1889) thousands of tons of cement have been manufactured, and the whole of this cement has been strictly tested by this machine with nicety and satisfaction. These cements are made in all parts of the country, to a certain penetration number, previously determined as necessary according to the different uses of the cement.