

XXXIX.—ON THE CONSTITUTION OF ULTRAMARINE.

BY H. ENDEMANN, PH.D.

The delay which has occurred in the publication of the *JOURNAL OF THE AMERICAN CHEMICAL SOCIETY*, coupled with the facts that the article, as originally written, has been published already in the *Chemical News*, and that Mr. Carl Heumann has attacked these views in the *Chemische Industrie*, makes it desirable that I should enlarge it with respect to some points, while it may bear condensation in others. The paper, as originally written, pretended merely to give my views regarding the constitution of ultramarines with sufficient facts to convey my ideas to those who have made the study of ultramarine a specialty, leaving closer scrutiny to their own efforts.

I shall adhere to this plan now, but since Mr. Heumann has not only attempted to pervert my own writings, but also to call his own perversions absurd, I see myself compelled to put certain points more prominently before the readers. My views regarding the constitution of ultramarine were first formed in 1877, and in order to prove their correctness I made it my task to prepare compounds, which should unmistakably prove the existence and possibility of those bodies which I consider to be the cause of the unusual composition of ultramarine.

I commenced with the aluminium sulphides prepared by various methods, and being there unsuccessful for reasons readily understood by those who have tried to work with these substances, introduced one more metal into the reaction.

These experiments are not concluded. In 1879 I had to discontinue my work, and with the view of discontinuing it entirely, I published at last my views in 1880, working the subject out sufficiently to bear publication, by using the advances in our knowledge reached meanwhile by others, as far as they were accessible to me.

Many have been the attempts to account for the peculiar and high color of ultramarine. Some authors have looked upon certain impurities as the actual bearers of the color (iron sulphide), others speak of a blue modification of sulphur, and others again of silicium and aluminium sulphide in very fine dissemination throughout the mass, but without chemical combination with the balance of the constituents. Lately, apparently, it has become a matter of taste to abandon entirely the discussion of the derivation of color. The statement is made that this question cannot be decided, that it is impossible, for

instance, to state why certain salts of cobalt are red and certain salts of copper blue. Nobody has attempted to decide why certain copper salts are blue, but it must be acknowledged that in dealing with certain compounds of copper of blue color, constitutional peculiarities may be readily recognized in all of them, by which they may be easily distinguished from other salts of copper which are colorless. The color of the salt in doubtful cases is a very positive indicator with regard to the type from which the constitutional formula should be derived.

Heumann reasons in a similar manner (*Ann. Chem.*, 203, 207). He says: "Nobody enquires into the coloring principle of Prussian blue, though neither iron nor cyanogen are blue, and, as nitrogen and oxygen may unite to form the reddish-brown nitrogen dioxide, we may accept that the combination of a silicate with a sulphide may possess a blue color. The desire to define the coloring principle of ultramarine is, therefore, it is to be hoped, a question which hereafter will not be asked." Mr. Heumann seems here entirely to forget that he has failed to show how a sulphide may combine with a silicate.

Having this problem in view, the following propositions have been made:

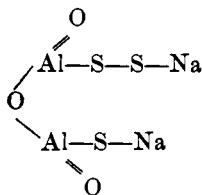
We are justified in insisting upon and foretelling for a colored compound an unusual grouping of the atoms, if its constituents, under the hitherto accepted arrangement of the atoms, would produce only colorless compounds.

If, in ultramarine, we consider the proportion of aluminium, silicon and sodium, to the non-metallic constituents, oxygen and sulphur, we find an excess of the latter.

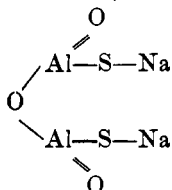
Aluminium is regarded as a tetratomic element. All ordinary aluminium compounds are assumed to contain two aluminium atoms linked together by two of their atomicities, leaving six atomicities for combination with other elements. There is a possibility of the existence of compounds without this binding of two atoms by one atomicity,—a possibility that compounds derived from the, as yet unknown, compounds AlO_2 and Al_2O_4 , may be prepared.

Considering the composition of ultramarine blue, we find that it consists of silica, soda, alumina, sodium monosulphide, and sulphur, the latter also in chemical combination, as it cannot be removed by solvents unless these at the same time act chemically. Most authors consider it as being united with sodium sulphide, forming polysulphurets. These substances, forming ultramarine, I do not, how-

ever, consider as serving all the same purpose. To simplify the explanation, I propose for the present to regard one portion of the soda and alumina and the whole of the silica, merely as a vehicle necessary for the preparation and existence of ultramarine, as they serve to facilitate the reactions in the first instance, while later in the process they may act in protecting the product against too powerful oxidation. This silicate may have a varying composition, and for this reason alone it would be difficult to correctly ascertain its quantitative relation to what may be called the *color nucleus*, i. e., the last group on the constitution of which the color of the ultramarine depends. This we can suppose in ordinary ultramarine blue to be:



and in Heumann's ultramarine blue (*Liebig's Annalen*, 203, 190):

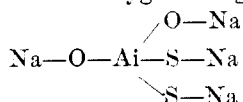


The first of the two, under the influence of acid, will give two-thirds of the sulphur as such, while one-third will be obtained as H_2S . The latter (Heumann's) will give half as sulphur and half as H_2S .

While, therefore, Heumann's ultramarine blue must be considered the purest, we see that ordinary ultramarine blue may contain more sulphur in chemical combination. How much sulphur may thus be added greatly depends upon the process of manufacturing the ultramarine, as I will show hereafter. A substance may therefore be a good blue, and yet analysis will give no fixed relations between the α and β sulphur, as mixtures of ultramarine rich and poor in sulphur may exist, and many analyses, which have been not generally accepted as correct, should not be rejected, provided the method of analysis which has been used, allows safe deductions to be made.

I. *Ultramarine White*.—The mother substance in the manufacture of blue ultramarine is ultramarine white. To it, as it is white, I assign a constitution analogous to that of the neutral sodium silicate,

a portion equal to half of the oxygen being substituted by sulphur.

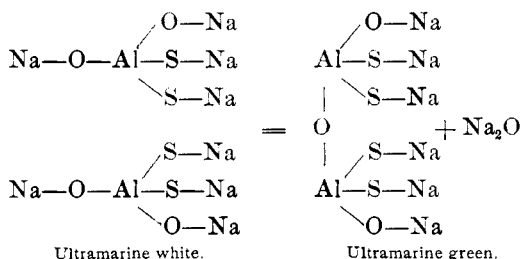


In giving this formula and all the others, I chose them merely as an illustration of the general principle involved in the discussion, and to enable me to convey my ideas, but not as absolute facts. The constitutional formula includes the possibility of partial substitution of aluminium by silicon. That, however, such a substitution takes place to any considerable extent is out of the question, since it would require a color nucleus containing no sodium, which according to our present knowledge of ultramarine is not possible. In the formation of ultramarine white, the presence of the large quantity of sulphur and soda appears as the cause of the breaking of the bond between the two aluminium atoms in alumina. Two molecules of this substance, acted upon by acids and water, will yield 1 sulphur and $3\text{H}_2\text{S}$, which corresponds with the best ultramarine white yet prepared (Ritter). Most ultramarine whites yield by the action of aqueous acids more free sulphur, but it will be readily seen that the above formula allows a ready interpolation of further sulphur atoms. Dry hydrochloric gas acting upon two molecules of ultramarine white produced directly ultramarine blue, chloride of sodium, water and sulphuretted hydrogen.

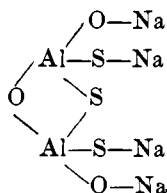


By the action of sulphurous acid gas, ultramarine white is first converted into ultramarine green, two atoms grouping together under loss of Na_2O , forming the first colored compound :

II. Ultramarine Green:

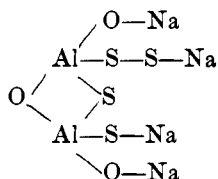


which then, by the action of oxygen, which forms sodium sulphate, under further loss of Na_2S , passes into the likewise green compound:



Aqueous acids, with the first green, would produce $3\text{H}_2\text{S}$ to S , and with the second green, $2\text{H}_2\text{S}$ to S . It is well known that ultramarine green contains rarely, if ever, the sulphur in such distribution; but this is easily explained by the assumption that these are derived from a white containing interpolated sulphur.

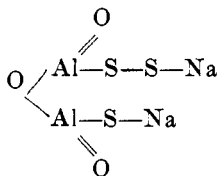
It is even possible that by the combined action of oxygen and sulphurous acid, an interpolated green may be obtained, the sulphur for the sulphate being then furnished by the sulphurous acid, so that in this case sodium alone is removed, leaving:



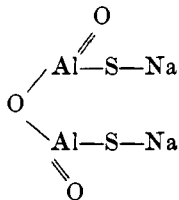
which compound, with aqueous acids, would yield $2\text{H}_2\text{S} + \text{S}_2$.

Gaseous dry HCl would produce all of these compounds, sodium chloride, and H_2S , leaving the blue on treatment with water in the insoluble residue, but this gas has perhaps rarely been used free from air and moisture, and the consequence has been that the reaction is generally accompanied by secondary ones. One of these would be that the mass would not lose so much in sulphur as is indicated by the above stated reaction. Another is indicated by the presence of aluminium chloride in the wash water, which is no doubt produced by water which is formed by the action of air on the hydrochloric gas. In the formation of blue from white directly, water is one of the products of the reaction, and in this case the formation of aluminium chloride is therefore unavoidable, and this substance is, therefore, a regular concomitant of the reaction.

III. *Ultramarine Blue* is, in the manufacture, produced by the action of sulphurous acid and oxygen on the green. Thereby more sodium is removed, and the middle sulphur interpolated in one of the groups ending with Na . The sodium is converted into sulphate. The action of chlorine will produce the same product, leaving:



This product should yield with aqueous acids $\text{H}_2\text{S} + \text{S}_2$. Hydrochloric acid gas would form $\text{H}_2\text{S} \cdot 2\text{NaCl}$, and



which latter substance, with aqueous acids, would yield $\text{H}_2\text{S} + \text{S}$.

This is Heumann's ultramarine blue, which in this degree of purity has only once been prepared, owing undoubtedly to the superior care used by Heumann in the production of this compound.

As regards the silicate rest, I will quote here an analysis, made about three years ago for the American Ultramarine Works, which gave the following results:

		Atomic Weight.	Atomic Relation.
SiO_2	39.28	: 60.0	0.655
Al_2O_3	26.41	: 102.8	0.257
Na_2O	20.83	: 62.0	0.336
S	12.98	: 32.0	0.406

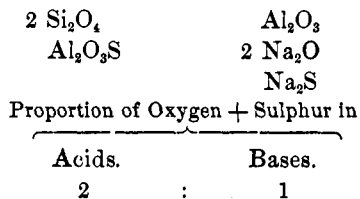
The sulphur being in two forms, two-thirds being obtained as S while one-third was obtained as H_2S , we divide 0.406 by 3, which gives $0.135 = 1$ atom of sulphur. For $\text{S}_2 = 0.406$ we require $\text{Na}_2\text{O} = 0.135$, and $\text{Al}_2\text{O}_3 = 0.135$ for the color nucleus. This leaves for the silicate:

Na_2O	0.201
Al_2O_3	0.122
SiO_2	0.655

or about $3\text{Al}_2\text{O}_3 \cdot 5\text{Na}_2\text{O} \cdot 0.16\text{SiO}_2$.

The complex character of this formula shows the difficulty which we would encounter in introducing the silicate rest into the formula.

Heumann found for this purest ultramarine the following formula : $2\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8 + \text{Na}_2\text{S}_2$, which, written according to my view, would be



In the above formula, $2\text{Si}_2\text{O}_4.\text{Al}_2\text{O}_3.2\text{Na}_2\text{O}$ represents what I have called the silicate rest, while $\text{Al}_2\text{O}_3\text{S}.\text{Na}_2\text{S}$ is the so called color nucleus, which, when introduced into the composition of a silicate, will produce a colored compound, even if it be not colored itself.

Since the question of the constitution of ultramarine resolves itself mainly into the determination of the position of the sulphur atoms, my action in considering a certain part of the molecule separately may be justified.

NEW YORK, March 14th, 1881.

XL.—THE ROTATORY POWER OF COMMERCIAL GLUCOSE AND GRAPE SUGAR. A METHOD OF DETERMINING THE AMOUNT OF REDUCING SUBSTANCE PRESENT, BY THE POLARISCOPE.

By Prof. H. W. WILEY.

In "the trade" the name of grape sugar is applied only to the solid product obtained from corn starch. On the other hand, the term "glucose" is given to the thick syrup made from the same material.

I shall use these words in their commercial sense.

INSTRUMENTS EMPLOYED.

I used in the following investigations two polariscopes, made by Franz Schmidt and Haensch, Berlin. The readings of these instruments, after correction for displacement, agreed well together.

The one was the instrument ordinarily used, in which the purple ray is employed, and the quartz half moons give blue and red tints.

Both of these instruments are graduated to read 100 divisions, each equal to 1 per cent. sugar with a solution containing 26.048 grms pure cane sugar in 100 c.c. In addition to this scale the half shadow has another which gives the actual angular rotation.