

## SALT-CAKE IN DYEING.

Written for the Scientific American by DR. M. REIMANN.

In England, as well as in Germany, salt-cake, or sulphate of soda, has been employed for some considerable time already as an expedient in dyeing wool.

The practical dyer, when asked concerning the advantages of this substance, which seems to possess so little importance, for the dyeing process, can state no reasonable ground for its employment, only in rare cases you will perhaps hear that the bath dyes more equally when sulphate of soda is added to it. Even the chemist, on regarding the matter somewhat superficially, does not observe what purpose the sulphate of soda serves in the dyer's bath. He considers it one of the number of utterly useless substances employed by the dyers in accordance with the prescriptions of some hand-book.

Nevertheless, if we regard the matter carefully in the following discussion, we shall see that sulphate of soda can be of the very greatest value in dyeing processes, and that its employment is based on the most interesting chemical and physical principles. At the same time we shall be obliged to advance into the comparatively unknown region of the dyeing theory, the practical use of which we shall soon recognize.

The sulphate of soda, which is scarcely ever treated of in books on dyeing, because of its chemical indifference for coloring matters, elevates, as every soluble substance does, the specific weight, and thus also the boiling point of the solution. This property already, when taken into consideration, renders it important for many dyeing processes. It is possible, for instance, to change the shade of aniline violet into blue or red, according as the temperature of the solution is more or less elevated.

When the dyeing is performed in an acid bath (the dyers very frequently add sulphuric acid to their baths), the sulphate of soda combines with the free sulphuric acid in the bath, and forms with it bisulphate of soda, a crystallizable solid salt. In this manner the bath retains its acid reaction without the presence of free sulphuric acid in the bath. Hence, when half-woolen cloths are dyed, the cotton in them, extremely sensitive to the action of the mineral acids, will be very well preserved.

Dissolved in water in great quantities, the sulphate of soda diminishes the capacity of the bath to dissolve the added coloring matters in as great a degree as though there were no such salt present; this, too, is highly important for many dyeing processes.

Several practical examples will demonstrate the advantages of sulphate of soda more conclusively than a whole series of theoretical observations. The red coloring matters as the cudbear, and more especially the magenta, and the red dyeing woods, possess, as is well known, the property of combining only with the greatest difficulty with the fiber when dyed in an acid bath. Therefore, wherever the substances are employed in the acid bath—and often this is necessary—the greatest part of the coloring matter is wasted and lost if the common process is employed. The same applies also to the yellow wood.

If, however, the said coloring matters be dyed in an acid bath according to this new method, a twofold result will be attained. By adding sulphuric acid, the dyeing power of the said pigments can be put into activity, and by varying the quantity of sulphate of soda which is employed, it is possible to control the combination of the pigment with the textile fiber. Therefore, by means of the sulphate of soda various shades can be produced.

This fact is of great importance in many sorts of dyeing. There are some kinds of yarn, especially the long *slubbing* wool, which have the property of felting when exposed too frequently to a change of temperature; they can then no longer be worked into weft yarn. Nevertheless, the wool must be exposed to such a change of temperature, for, in preparing the shades, it is taken out of the bath at times, so that new coloring matter may be added to the part already in the bath.

In all these cases it would be unnecessary to take out the yarn if we were to add a little more coloring matter and acid, and shades could be produced by gradually adding sulphate of soda to the bath. By this process a great deal of manual labor may be spared, and the dyer enabled to work with far more security and comfort. Should at any time too much coloring matter have gone upon the fiber, the fault can readily be corrected by the addition of a little acid.

The truth of the above assertions is most easily perceptible in dyeing Magenta. As another example, let us regard the dyeing of shades, for which the wool must first be boiled in a solution of a chrome salt, in the most cases in bichromate of potash. This is often done for red, brown, and gray, which are produced by means of logwood, red and yellow wood. When the wood is boiled in a bath of bichromate of potash, and especially when to this, as is commonly the practice, sulphuric acid is added, the colors of the logwood and red wood attack the fiber very quickly, and therefore often spread unequally. Hence, dyers must begin to dye at low temperatures, and must increase the heat very slowly. If to such a dyeing bath but a small quantity of acid is added, the effect of the coloring matters in it is almost nothing, it is, therefore, possible to dye with the boiling bath without fear of an unequal spreading of the coloring matters. It is only necessary to add, while the coloring matter is fixing on the fiber, sulphate of soda in small quantities, the coloring matter will combine with the fiber, while the sulphate of soda absorbs the free acid. It is therefore possible to produce shades without removing the goods from the bath, if we take care that the quantity of coloring matter which is at first added to the bath is not too small.

A similar effect can be produced by adding the sulphate of

soda at the beginning of the dyeing process. For sulphate of soda we may, in this case, employ even common salt. In this case the salts employed will, when dissolved in the fluid, precipitate the dissolved coloring matter, which is then contained in the bath, in a very fine state of division, or the salts will prevent the coloring matters from dissolving, according as these latter or the salts were first introduced into the bath.

For the process this is quite indifferent. The pigments fix on the fiber in the same measure as they are dissolved. Fresh coloring matter will only then be dissolved, when the portion already in dissolution is already consumed. The dyeing is more equal, if the coloring matters are not dissolved in the bath, but are contained in it in a state of minute division, as every dyer knows who has ever employed aniline blue, soluble in water. This pigment, because of its ready solubility in acids, often fixes too quickly if the dyeing is carried on in an acid bath, and therefore dyes at times unequally. It is therefore best to dye from a neutral or weak alkaline fluid, and then to produce the blue by adding an acid. The same pigment soluble only in alcohol is precipitated as soon as its solution is added to the bath, and therefore dyed more equally, though more slowly still. In many cases also it is advantageous to employ sulphate of soda where small quantities of indigo carmine are used to give somewhat more of blue to a shade. The affinity of this coloring matter for wool being very great, small quantities of it may often dye the woolen goods very unequally; to prevent this, and give uniformity to the color, it is necessary to continue the boiling operation for some time. The indigo carmine will dye more slowly and equally in the case of the free acid is carried off by sulphate of soda.

The question now remains whether only the sulphate of soda, the importance of which I have endeavored to prove in the preceding remarks, is able to produce these results, or whether any other agent, can replace it in these processes.

In the preceding I already mentioned common salt as a substitute; and it can be advantageously employed, if either a higher specific weight can be produced, or the dissolved coloring matter be precipitated.

When common salt is employed in an acid bath, the development of hydrochloric acid is highly disagreeable. Cotton is violently attacked by it. Common salt can in turn be replaced for these processes by sulphate of magnesia and other salts which exercise no effect on the chemical constituents of the coloring matters, as, for instance, the compounds of alumina, iron, and tin.

Similar to the effect produced by the sulphate of soda, is that of the corresponding combination with potash, viz.: the sulphate of potash. This salt, however, is more expensive than the soda-salt. The bisulphate of potash is now already frequently employed in dyeing. The bisulphate of soda, which is a residuum in some chemical manufacturing processes, for instance, in the production of nitric acid can often be advantageously employed for sulphate of soda and free acid.

To compare the expense of the employment of these substances, we must therefore observe that the sulphate of potash crystallizes without water, while the sulphate of soda contains 55.9 per cent, and the sulphate of magnesia 51.22 per cent of water, which is of course devoid of any value.

Finally, we must state that 100 parts of crystallized sulphate of soda are able to fix 30½ parts of sulphuric acid (of 668 B. s. w.), and thus to form bisulphate of soda; or, in other words, for every pound of sulphuric acid added to the bath, three pounds of crystals of sulphate of soda must be employed.

## MANGANESE—ITS USEFUL APPLICATIONS IN THE ARTS.

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This mineral substance was known in ancient times under the name of "glassmaker's soap" and was considered a species of iron ore. In the year 1740 it was ascertained to be an oxide of a separate metal, and in 1774, Gahn obtained the pure metal from the native carbonate, exposing the same to intense heat for several hours, or by subjecting chloride of manganese to electrolysis. Boerhaave does not appear to have known the metal. In my English edition of 1753 he speaks of it in the following words: "Take the frit and set it in melting pots in a working furnace, adding in each pot a proper quantity of a blackish stone not unlike loadstone, and called manganese, which serves to purge off that greenish cast natural to all glass and to make it clear." Scheele, Bergman, Chevreul, Berthier, and Berzelius, have in modern times investigated the physical and chemical characters of manganese. The ore is widely distributed over our globe; it accompanies many iron ores, particularly the hematites, also the franklinite of New Jersey. It has been detected as a constituent of meteoric iron in the ashes of most vegetable and many animal substances, is the coloring principle of many fossils in a dendritic form in the chalcidony which is called the "mocha stone," and in the same form on sand pebbles of which I found plenty in Stanislaus River in California. It also occurs combined with sulphur, carbonic acid, silica, water, and with many atomic proportions of oxygen, such as protoxide, sesquioxide, binoxide, manganic acid, and permanganic acid becoming thereby sometimes a base and sometimes an acid. The principal varieties of manganese found in nature are of the following descriptions:

- 1st. Hausmannite has the form of a four-sided pyramidal crystal, with hardness 5, and a specific gravity 4.7.
- 2d. Braunite is an anhydrous sesquioxide, crystallizes in an octahedron, is much harder than the last, and has a higher specific gravity.
- 3d. Psilomelane, generally called the compact gray oxide, occurs in botryoidal and stalactitic shapes.
- 4th. Manganite is a hydrous sesquioxide; crystallizes in right rhombic prisms.

5th. Pyrolusite, the most useful and abundant ore of manganese, derives its name from two Greek words signifying "fire" and "to wash", in allusion to its property of discharging the brown and green tints of glass; it crystallizes in small rectangular prisms, or is fibrous, radiated, and divergent, of iron black color and grayish streak, has a specific gravity of 4.94, and is composed of 37 per cent oxygen and 63 per cent manganese. This ore is generally called binoxide, deutoxide, or peroxide, is a good conductor of electricity, and strongly electro-negative in the voltaic circuit. When heated to redness it readily parts with its excess of oxygen as it gives off one third of it. When heated with sulphuric acid one half of its oxygen escapes. Owing to this property it is more employed in the arts than any other oxide; it is called in trade the "black oxide of manganese." Its commercial value is dependant upon the proportion of oxygen which it contains in excess of that which is necessary to its existence as sesquioxide. A convenient method of estimating this excess of oxygen is founded upon the circumstance, that the black oxide of manganese is decomposed in the presence of oxalic acid, and from sulphuric acid proto-sulphate of manganese is formed, and all the excess of oxygen reacts upon the oxalic acid and converts it into carbonic acid which passes off with effervescence. If the mixture be weighed before the decomposition has been effected, and again after it has been completed, the loss will indicate the amount of carbonic acid; each equivalent of peroxide of manganese gives two equivalents or its own weight of carbonic acid.

Manganic acid is known under the name of chameleon mineral, is obtained artificially by fusing the peroxide of manganese with equal weights of caustic potash, which when dissolved in a small quantity of water has a green color, but when largely diluted becomes purple and ultimately claret color; for this property it has been employed for many years in the arts.

Permanganic acid is artificially obtained by mixing intimately four parts of finely powdered peroxide of manganese with three and one half parts of chlorate of potash, while five parts of hydrate of potash are dissolved in a small quantity of water and added to the above mixture, the whole is evaporated and reduced to powder, then heated to dull redness for an hour in an earthen crucible and when cold the mass is treated with water and filtered through a funnel plugged with asbestos; the solution after being neutralized with sulphuric acid yields on evaporation beautiful red acicular crystals of permanganate of potash. This preparation of later years has become an important vehicle for disinfection. Among the other native oxides of manganese may be mentioned the *mineral acid* which is also very abundant but not valuable enough to produce gas. It is amorphous, soft, black, or brown and purple; when mixed with linseed oil it produces spontaneous combustion. It is supposed to be the coloring ingredient of the dendritic delineations upon many substances, such as steatite and others mentioned elsewhere. The localities of manganese are very prolific; pyrolusite has been mined very extensively in Europe; psilomelan in England, France, Belgium, and the United States; manganite in Bohemia, Saxony, and England. Much of the latter is consumed in the bleacheries of those countries. The United States and the Provinces have inexhaustible deposits of the oxides of manganese. From Vermont, the eastern limit, to Georgia, the southern limit, large supplies were formerly furnished, but in late years West Virginia, North Carolina, and California have supplied us to a large extent but not of a high grade of oxidation. While the binoxide of manganese suitable for the manufactures ought to yield from 80 to 90 per cent of oxygen gas, the product of the last mentioned States has not exceeded 50 to 70 per cent oxygen. The provinces of New Brunswick and Nova Scotia have produced within a few years very superior oxides of manganese, and the specimens I possess in my cabinet excel in richness and beauty those from Ilmuran in Thuringen and Ihlefeld in the Hartz mountains of days gone by. The manufacturers of bleaching powders in England have for the last twenty years been supplied by the little principality of Nassau to the amount of fifty thousand tons per annum, while the United States with all its inexhaustible resources has not exported any, and it is hoped that before long the export of manganese may prove lucrative. The quality of the Nova Scotia manganese is, according to Howe, of high percentage, some from 82.4 to 89.8 of sesquioxide, and that from Tennycape as high as 97.04. The international manganese mine of New Brunswick contains from 80 to 85 per cent of sesquioxide. We find manganese in the State of Missouri containing much cobalt, while the Vermont manganese is associated with much iron. We also find in California, in the red hill of the bay facing the city of San Francisco, containing millions of tons of psilomelane or compact manganese yielding from 40 to 50 per cent sesquioxide. We also know manganese to be abundant in Canada. A vein of 50 to 60 feet wide is said to exist at Bachawanning Bay on Lake Superior.

The geological position of manganese is not quite accurately known. In Germany it traverses porphyry and is associated with calcspar and baryta. In Vermont, in the United States, it is found among crystalline rocks; in Canada it is accompanied by dolomite, and in Nova Scotia it exists in a gray limestone, quartzite, and conglomerite, and it unquestionably belongs to the new red sandstone formation. My manganese mines at Pembroke are situated close to the gypsum deposits, which would range them with the upper silurian system.

I will now enumerate the many useful applications in the arts.

1st. Manganese is employed for producing oxygen gas in the chemical laboratory, the material of the compound blow pipe and drummond light, for the production of alkaline manganate in order to procure a good and cheap light in combination with coal gas.