chamber and washed away with the waste water, giving a supply of clean air in the shop. Also, the temperature of the shop room may be maintained at a uniform degree and in summer, when high temperatures prevail outside, the shop may be kept at lower and more comfortable temperatures.

Although developed primarily for use in wood-using establishments, first in the dry kiln and then in shops and storage rooms, the field of this humidity and temperature control is by no means restricted to wood-working plants. It may be used wherever for any purpose it may be found desirable

to maintain definite, uniform atmospheric conditions.

Among others, conditioning control has been found beneficial both to the material being manufactured and to the health of employes in the following places: Finishing and drying rooms, textile mills, munition factories, chemical factories, foodstuff factories, rubber factories, and tobacco factories. There are numerous other important industrial plants in which control of atmospheric conditions would be beneficial and the type of apparatus described in this article would probably be applicable to many of them.

General Applications of Selenium—1*

Its Utilization in Biological Chemistry and in the Glass and Rubber Industries

By Louis Ancell

AT first glance selenium and its applications hardly seem to be properly included within the domain of industrial chemistry properly so-called. However, certain new applications of this metalloid either already accomplished or by way of accomplishment in biological chemistry, in chemical industry, and especially in electrical technology make it a matter of interest to consider in a single article the properties and applications—at once so original and so varied—of this substance so scantily found upon the earth and yet so well-known because of the numerous scientific works devoted to it.

We will examine in order:

1. Selenium and its principal properties.
2. The utilization of selenium in biological chemistry.
3. The employment of selenium in the glass and rubber industry.
4. The applications of selenium in electrical technology, especially in the chemical industry, the military art, the photography of words or the reproduction of sounds by photography, wireless telephony, television and the transmission of images to a distance, and photometry.
5. The future of selenium and its applications.

Selenium is best known by its curious property of having its electric conductivity influenced by exposure to light, but it is none the less true that it is capable of various chemical applications of an industrial nature, and in this respect it offers a wide field for research.

PRINCIPAL PROPERTIES OF SELENIUM.

Manufacture.—Selenium is a metalloid belonging to the sulphur family whose atomic mass is 79.1, the figure adopted in 1898 by the International Commission of Atomic Weights. It was discovered in 1817 by Berzelius in the sediment of the lead chambers of Gripsholm, the treatment required being long and complicated. The present process as applied in one of the principal chemical works in France, consists in extracting the selenium from the residuum left by the treatment of the Hautmont (Nord) pyrites, titrating about 15 per cent. These residues are first treated with *aqua regis* which transforms the selenium into selenious acid. This latter compound is reduced by sulphurous acid which precipitates the selenium in the form of a powder which is then washed and dried. Finally the product is melted and run off in the form of cylinders in copper molds immersed in water; it is placed upon the market in this state.

Selenium can also be extracted from zorgite and the impure double selenide of copper and lead which is tolerably abundant in the Argentine Republic, and which contains nearly 30 per cent of selenium. In this case the pulverized mineral is

treated with *aqua regis* which transforms the selenium into selenious acid and the metals into chlorides. The excess acid is driven off by evaporation and the sirupy liquid is then diluted with water in order to precipitate the major portion of the chloride of lead. After filtration the clear liquid is treated by a current of sulphurous gas which precipitates the selenium in the form of red flocculae. It is filtered again and washed with hydrochloric acid and with water to eliminate the last traces of chloride and is then melted in black lead crucibles and run off either in sheets or in cooled molds.

It is of importance, especially with respect to the physical applications of selenium, to purify it in order to eliminate the sulphur and the tellurium which it always contains. One of the most practical methods of doing this appears to be that of Divers and Shimosé¹ since this permits a rapid and practically complete purification. In this process the selenium is dissolved in boiling concentrated sulphuric acid and is thus transformed into selenious acid. The cooled liquid is afterwards diluted with water and then treated with a current of sulphurous gas which precipitates the selenium. The red powder obtained is separated by filtration, washed with water and alcohol, and then placed to dry upon plates of porous porcelain. In this manner the traces of tellurium are completely eliminated and the purified product contains only slight traces of sulphur which are practically negligible.

Selenium presents itself in various allotropic conditions which are of interest because of their peculiar properties. A first form of these includes vitreous selenium, amorphous selenium, and colloidal selenium; a second form is red crystallized selenium; and a third form is grey or metallic crystallized selenium which is differentiated from the other two forms by the fact that it alone is completely insoluble in carbon disulphide.

Vitreous Selenium.—1. In its first form selenium melts at 220° C.; and becomes soft and viscous at about 60° C.; if it is then cooled again it becomes hard and brittle and is then called *vitreous* selenium. This is black in color with a conchoidal fracture and when powdered it is grayish if the powder is coarse, and red if it is very fine. In the course of our researches (begun in 1909) concerning this variety, we found that vitreous selenium melted at 220° C. and when cooled rapidly *under pressure* is suddenly transformed into a new variety, *violet* gray in color and composed of fine crystals which are highly sensitive from the photo-electric point of view, but whose stability leaves much to be desired. In order to utilize and preserve this extra sensitive variety, consequently, it is advisable to add to it a certain quantity of vitreous selenium in order to distribute uniformly the violet gray crystals in a sort of solid and stable solution of vitreous selenium. The latter constitutes a substratum which cements and re-

*Translated for the SCIENTIFIC AMERICAN MONTHLY from *Chimie et Industrie* (Paris).

¹Divers and Shimosé, *Chemical News*, Vol. 51, p. 199, 1885.

unites the various sensitive crystals of the upper stratum which is exposed to the light. Accepting this explanation which appears to be more or less plausible but which is given here merely by way of suggestion, we succeeded in discovering a process which enabled us to make a practical preparation of selenium cells which are extremely sensitive even to the feeblest luminous intensities. On the other hand the slightest impurity (particularly metallic powders) constitutes a sort of poison, which while activating the transformation causes the destruction of the unstable variety of sensitive crystals and transforms the mass of selenium into a variety which is as good a conductor as a metal, and is furthermore insensitive to light.² This modification is also capable of being produced in the cells by the mere lapse of time, or under some external influence such as the sudden passage from heat to cold or vice versa, a somewhat violent shock, or a sudden break of a circuit containing a self-induction and the cell. It is obvious, therefore, that very great precautions must be taken in the preparation as well as in the employment of this variety of highly sensitive selenium.

Amorphous Selenium.—Also included in the first form of the allotropic state is *amorphous selenium*, which is obtained in the state of a red precipitate through the reduction of selenious acid by sulphurous gas. Heated to a temperature of 40° C. to 50° C. this red powder becomes agglomerated into a soft mass, which becomes hard and brittle when cool.

Colloidal Selenium.—Colloidal selenium, the third variety of this first form is obtained by mixing two very dilute solutions of selenious and sulphurous acids. The mixture, which is yellow at the beginning, gradually turns red and finally deposits a red powder of selenium, insoluble in water, which becomes agglomerated at 40° C. to 50° C., and is transformed like the amorphous selenium, and under the same conditions, into vitreous selenium.

Crystallized Red Selenium.—2. This constitutes the second form of the allotropic state. It is not sensitive to light and is obtained by the slow and careful evaporation of a sulpho-carbonic solution of selenium.

Crystallized Selenium.—3. Finally *gray or metallic crystallized selenium* is obtained by the action of heat upon any one whatever of the foregoing varieties. This according to Saunders³ is the form which is most stable at all temperatures below 217° C. to 220° C., the point of fusion of selenium. This variety is not soluble in the sulphide of carbon, no longer exhibits a conchoidal fracture, and assumes a granular aspect; it is a conductor of electricity especially under the influence of light or of a slight elevation of temperature.

The density of selenium varies from 4.259 to 4.805 in the different varieties.⁴

The average boiling point of selenium is about 690° C. as proved by Daniel Berthelot.⁵

Vitreous selenium which is not a conductor of electricity is transformed as we have seen under the influence of heat alone into the metallic conducting modification, or under the combined influence of heat and pressure⁶ into a modification which is an even better conductor of electricity than the ordinary metallic variety. This conductivity is highly augmented when the selenium is mixed with metallic powders. It is well to note, also, that the heating of selenium in order to obtain a highly sensitive variety should be made with a care to exclude both humidity and a direct gas flame.

The augmentation of the conductivity appears to be due to the presence of metallic seleniides according to the researches of a number of authorities (Graham Bell, 1880, Schuller, 1883, and Bidwell, 1891), corroborated by our own investi-

gations. When these seleniides are formed upon the surface of wires or of sheets the conductivity is normal; when, on the contrary, a few fragments of metallic powders or of vitreous selenium which has been melted and previously rubbed upon the metal, are mixed with pure vitreous selenium the latter is transformed under the influence of heat alone, or still more rapidly under the combined influence of heat and pressure into a variety of selenium which is so good a conductor that its conductivity approximates that of a metal. A cell sensitized under these conditions is practically unusable. As a result of this fact in constructing selenium cells it is necessary to employ a support which contains not the slightest metallic or conducting particle and which is incapable of absorbing humidity. Porcelain and certain varieties of steatite are suitable for this purpose.

The nature of the metal employed as an electrode does not appear to have any perceptible influence upon the conductivity of the selenium. Platinum has the advantage of not being readily oxidized and copper or even brass can be readily used in practice.

We may mention here that a collation of all the researches devoted to selenium has been undertaken in various quarters (Amaduzzi, 1904; Marc, 1907; and Ries, 1908). The Russian journal *Questions de Physique* for 1910, page 175, contains a résumé of the principal results obtained.

THE UTILIZATION OF SELENIUM IN BIOLOGICAL CHEMISTRY.

Selenium alone has hitherto found but little employment in chemistry worth mentioning from the industrial point of view. But it has been used for several years in the form of cutaneous injections in mice at the Institut Pasteur by M. Borel, in certain biological researches relating to the development of cancer. It has been thought that the toxicity of selenium and of its salts might occasion a retrogression of the tumors. As a matter of fact, however, the experiments made upon mice have not yielded conclusive results and no tests have been made upon human subjects. So far as we know no new researches have been attempted along this line.

SELENIUM IN THE GLASS AND RUBBER INDUSTRIES.

Selenium has been employed in the manufacture of glass, giving a pale violet color and more recently in the vulcanization of rubber.

In the first case the selenium is incorporated with the molten glass, either in the form of vitreous selenium or under that of selenites which undergo reduction during the manufacture of the glass.

As regards the latter use experiments have been conducted in Boston since 1913 by the Simplex Wire and Cable Co. In these experiments a quantity of selenium equal to that of the sulphur employed in ordinary vulcanization is heated to 150° C. for two hours' time. The product obtained is somewhat less solid from the mechanical point of view than the rubber vulcanized by sulphur. On the other hand it is possible to obtain selenium rubbers which are soft and very durable and which exhibit excellent resistance to normal traction and extension by heating the selenium to 135° C. together with certain organic accelerators for a period of time twice that of ordinary vulcanization.

This selenium caoutchouc does not deteriorate in spite of the sensitiveness of selenium to light.

(To be continued)

NEW USES FOR "CELLON."

LIQUID "Cellon" can be used for impregnating textiles, etc., or for making insulating tape. In this latter form it can be taken from the round box in which it is wound up, even in the moist condition, and allowed to harden in air.—Abstracted through *The Technical Reviews* from *Mitteilungen des Reichsbundes Deutscher Technik*, Aug. 30, 1919.

¹Louis AnceI, Bull. de la Soc. Chimique (Chemical) de France, fourth series, Vol. xvii, p. 10, 1915.

²Saunders, Jour. of Phys. Chem., Vol. iv, p. 423, 1900.

³Schaffgotsch, Journ. f. prakt. Chm. Journal of Practical Chemistry, Vol. xlii, p. 308, 1848.

⁴D. Berthelot, C.R. Ac. Fr., Vol. 134, p. 705, 1902.

⁵Louis AnceI, Bull. Soc. Chim. 1c.