greatest possible approximation, cemented zones possessing the characteristics required by the mechanical constructor, who alone can know with precision the nature of the service to which the cemented and hardened pieces are to be subjected.

Summarizing, we may say that the methods of control spoken of permit of determining the following principal defects which may present themselves in the cemented and hardened pieces, and, in the majority of cases, of recognizing their causes:

1. Excess or deficiency in carburization.
2. Insufficient protection of the regions which are not to be cemented.
3. Sudden variations in the concentration of the carbon in the successive layers of the cemented zone.
4. Lack of uniformity in the cemented zone.
5. Deformations of the pieces after the cementation and after the hardening.
6. Inequalities in the temperature.
7. Excess or deficiency of hardening.
8. Cracks in the cemented and hardened zone.
9. Brittleness of the cemented and hardened zone (tendency to exfoliation, etc.)
10. Brittleness of the "core" of the cemented pieces.

The causes of these troubles and the means of remedying them are in part extremely easy to perceive; thus, for example, it is hardly necessary to say that when a cemented piece is too soft owing to deficiency of hardening it is necessary to quench it more energetically. In other cases, the observations and tests fully discussed in the first and second parts of this volume are sufficient to reveal their causes and their remedies. To cite two examples, the causes and the remedies of an excess or a deficiency in the concentration of the carbon in the cemented zones are explained by the phenomena of chemical equilibrium during the processes of cementation; and those of an irregularity in the intensity of the cementation in the various parts of a piece, due to irregularities in the heating, are clearly explained by the effects of temperature on the velocity of the cementation.

# CHAPTER V

## SOME PATENTS CONCERNING PROCESSES FOR THE CEMENTATION OF IRON AND STEEL

In the preceding chapters we have cited several times rules and data contained in some patents. But desiring to limit ourselves to the study of cementation proper, we have cited only patents concerning processes on which quite precise and sure data were known. In fact, with a few exceptions we have limited ourselves to reporting quantitative data whose exactness was based on our own experimental investigations, or because they had been directly observed by us in practice.

But this is possible for only a limited number of the processes of cementation patented in various countries. In the majority of cases, in fact, the descriptions accompanying the claims constituting the essential part of the patents are written with every care to avoid disclosing the best way of usefully carrying out the claims in practice. From the point of view of the inventor it would appear sufficient that a description should contain the correct directions, but mixed with any amount of useless data; so that in case of a legal contest it can be maintained that the correct directions were really given.

We will, however, refer briefly to some patents whose true practical value is unknown to us, either for the reasons just referred to or because, although the descriptions furnished are clear and simple, we have not been able personally to test their results nor to obtain information from any one who has tested them. We will limit this review to reporting from many such a few examples adapted to show some of the directions in which inventors have entered this field.

Many inventors have attempted to increase the activity of the carburizing mixtures by the addition of the most varied substances, in the choice of which it is sometimes difficult to find the guiding principle or any reasoning based on well ascertained facts.

One of the substances whose addition to the cementation powders is most frequently proposed is borax. Thus, Th. Langer proposes (German patent, No. 55544, Kl. 18, 1891) the following mixture:

| | |
|---|---|
| Common salt | 15 parts |
| Yellow prussiate of potassium | 5 parts |
| Borax | 1 part |

or the other:

| | |
|---|---|
| Common salt | 3.2 parts |
| Yellow prussiate of potassium | 0.3 part |
| Charred horn parings | 0.5 part |
| Borax | 0.07 part |

As is seen, the inventor considers that the borax exercises its action even when used in quite small proportions.

The same remarks may be repeated for the following mixture proposed by Gallet (United States patent, No. 146330, 1874):

| | | | |
|---|---|---|---|
| 1. Alumina, from | 0.5 | to | 1 gram |
| 2. Highly aluminous clay | 12 | to | 20 grams |
| 3. Pulverized wood charcoal and lamp black | | | 50 grams |
| 4. Calcium carbonate | 38 | to | 42 grams |
| 5. Potassium carbonate | 18 | to | 30 grams |
| 6. Sodium carbonate | | | 2 grams |
| 7. Caustic potash | 0.5 | to | 1 gram |
| 8. Manganese oxide | | | 4 grams |
| 9. "Rosin" | 4 | to | 5 grams |
| 10. Common salt | | | 1 gram |
| 11. Sal ammoniac | 0.5 | to | 1 gram |
| 12. Borax | 0.5 | to | 1 gram |
| 13. Water | about 10 per cent. of total weight | | |

In this powder, which constitutes an interesting example of those complex mixtures referred to several times in the preceding chapter, not only the borax but even several of the other substances are present in homeopathic doses. Thus, the question naturally arises as to what specific efficacy half a gram of alumina can have along with 12 grams of clay, or 2 grams of sodium carbonate along with 18 or 30 grams of potassium carbonate.

Another mixture of the same kind is the following, proposed by F. G. Bates (German patent, No. 83093, Kl. 18, 1895):

| | |
|---|---|
| Carbon | 90 parts |
| Cryolite | 10 parts |
| Manganese oxide | 20 parts |
| Common salt | 1 part |
| Saltpeter | 1 part |
| Spent lime | 10 parts |
| Alum | 10 parts |

That 1 gram of common salt must truly be of great importance in such a mixture!

Just as curious is the mixture patented by F. André (see English patent, No. 1356, 1906), composed of potassium ferrocyanide, hide clippings, wood charcoal, resin, soda, earth, saltpeter and graphite. And that patented by Cattaneo and Faggian (see English patent, No. 13931, 1906), containing



scrapings of ox horns, prussiate of potash, Peruvian bark, potassium bichromate, common salt, saltpeter, tartaric acid, boric acid, sal ammoniac, sulphuric acid, resin or colophony, magnesia, sawdust, carbon and soot.

Then, there are not lacking inventors who indicate in detail the special virtues of each of the ingredients of their complex mixtures. Thus, John Buckland Jenkins (United States patent, No. 490660, 1898) says (p. 1, lines 37–47) that his "compound" is formed of the following "reagents:" "A carbonaceous substance, such as wood charcoal, which imparts hardness to the product; manganese dioxide, which produces malleability and ductility; sodium chloride, which softens and gives tenacity; potassium cyanide, which hardens and makes the steel take the temper better; and ammonium chloride, which serves the same purpose as the potassium cyanide but costs less and is therefore used in greater proportions, nitrogen being the essential element." The sureness and the precision with which Mr. John Buckland Jenkins has succeeded in distributing the various functions among the various constituents of his mixture must certainly arouse envy in every experimenter.

We could continue for many and many a page the list of patented cementation mixtures like those reported above, but having our doubts of the usefulness of completing such a list, we forbear.

We will cite only one other example, which confirms the fact that many of the descriptions filed with applications for patents are skilfully written in a purposely uncertain and inexact way, so as to make it impossible for any one reading them to apply the process. The French patent No. 327984 of June, 1902 (Lecarme), proposes to prepare the cementing mass by the combination, in varying proportions, of the two following mixtures:

| | | |
|---|---|---|
| (*A*) | Wood charcoal in fine powder | 1 liter |
| | Concentrated aqueous solution of potassium cyanide | 1 liter |
| (*B*) | Powdered carbon | 1 liter |
| | Saturated solution of potassium ferrocyanide | 1 liter |

This mass is to be used either as a "varnish" (see p. 284) or, mixed with charcoal, to form the filling of the ordinary cementation boxes. Now, it is clear that a mixture containing such a large proportion of water could not be used in the usual cementation boxes without some special arrangement for permitting the easy escape of the great quantities of water vapor which would rapidly form in these boxes, nor without some means capable of preventing the harmful action which water vapor produces when evolved *in contact* with the surface of the pieces subjected to the treatment.

Various processes of cementation are based on the use of aqueous solutions of various carburizing substances.

These solutions are to be used by immersing in them the objects of steel at white heat; the objects are thus simultaneously cemented (as the result of the carburizing substances dissolved in the bath) and hardened by the sudden

cooling produced by the immersion in the liquid. Among the patents of this group is the English patent No. 2981, 1890 (M. F. Coomes and A. W. Hyde), which recommends the use of aqueous solutions of sugar, molasses, oxalic acid and alkali oxalates, tartaric acid, etc. The efficacy of processes of this kind is very doubtful.

There are, next, many other patents claiming the use of *one* well-defined substance which, used alone or added to the simplest cements of well-known action, produces rapid cementations. Among these patents, which in general are more worthy of notice than those of the preceding group, there are some which are certainly of no real practical importance. But, notwithstanding the large number of such patents, and the very great practical importance which they would have if they really gave practical results such as claimed by their inventors, I do not find that any of them have found practical application to any considerable extent. Besides this, in the few cases in which I have had occasion to try the substances designated in the patents of this group, I have not been able to obtain results better than those which are obtained with the cements ordinarily employed in all works.

Among these an example is that of Lamargese (English patent No. 25986, 1903), which claims the use of silica added to the wood charcoal of resinous plants.

Some experimental tests made to control the results of this mixture did not give results appreciably different from those obtained with other solid cements.

To the same group belong the patents of the "Cyanid-Gesellschaft" (see, for example, the English patent No. 16412, 1904, and the French one, No. 345642), claiming the use of cyanamide or of its compounds with the alkali or alkaline earth metals as cements. According to these patents, the mixture of eighty parts by weight of calcium cyanamide with twelve parts of wood charcoal is especially to be recommended. Guillet, who has tried these substances, has been able to establish [1] that they furnish results inferior to those which are obtained with the mixture of carbon and barium carbonate.

Thus, also, I do not find that there are at present employed, or at least not on a large scale, the processes patented by Engels (see, for example, the French patent No. 337154, 1903), which consist in using as cementing substance carbon silicide mixed with materials (such as sodium sulphate) capable, according to Engels, of assisting its decomposition.

Besides the means based on the choice of the carburizing material, other expedients have been studied to render the cementation more rapid. As an example, that patented in 1895 by A. Ammermann Ackermann (see German patent No. 79429, Kl. 18), consisting in hollowing out on the surface of the metal to be cemented a large number of grooves, of a depth proportioned to the

[1] *Génie Civil, loc. cit.*



thickness of the pieces to be cemented, placed close to each other in such a way as to completely cover this surface. In this way the surface on which the process of the penetration of the carbon by diffusion takes place is greatly increased and the quantity of the carbon which penetrates into the steel in the unit of time, all other conditions being equal, is likewise increased. The cementation being finished, the pieces are subjected, while hot, to a mechanical treatment (forging, rolling, etc.), capable of restoring to their surface its original form by leveling the ridges between the various grooves. The method was proposed by Ackermann especially for the cementation of plates, for which the restoration of the plane surface could be easily obtained by simple rolling of the rough ("grooved") cemented surface.

This procedure presents two serious disadvantages: the first, which it was easy to foresee, consists in the practical difficulty of rolling the grooved and highly carburized surface until it is again wholly plane, without harm to the qualities of homogeneity, compactness and continuity which are required of the metal of the cemented zones. The second disadvantage is that the cementation does not take place uniformly at all points of the surface but gives rise to a much more intense carburization of the edges in relief, for which the relation between the external surface (on which the cementation takes place) and the volume of the metal carburized as the result of a definite depth of penetration of the carbon is greatest. These differences between the concentrations of the carbon in the various parts of the metallic piece may attain very high values, especially if the grooves hollowed out on the surface of the steel are deep and numerous, and they cannot be eliminated practically by means of succeeding heat treatments. The regions thus super-carburized become brittle as the result of the hardening.

Another expedient proposed several times (see, for example, the English patent, Cowden, No. 13761, 1904) to obtain more rapid cementations than those which can be obtained by the usual processes consists in making the cementation begin as soon as the metal begins to solidify. Thus, in the process protected by the English patent just referred to, the steel is cast in a mold which, besides containing an arrangement designed to effect the enrichment of the steel in manganese only in some parts of it, is supplied with cavities filled with masses of carbon, the surface of which forms definite portions of the mold itself. In this way, the ingot of steel, which is obtained by casting the fused soft metal in such a mold, absorbs carbon only in those parts of its surface where the mold is composed of carbon. Moreover, the carburization of the metal should take place quite rapidly, as the diffusion of the carbon would begin at the surface of a mass of steel in the state of only incipient solidification. I do not find that this process, which the inventor indicates as being especially adapted to the manufacture of toothed wheels, is applied at present, and I have cited it only as an example of the numerous expedients proposed either to accelerate or to localize the cementation.

One of the means by which inventors have often tried to obtain rapid cementation is the use of electrical energy.

In the majority of cases the electrical phenomena are utilized only for their heating effect; but in other cases the inventors also try to utilize an assumed specific action of the electric current, which is supposed to behave as a carrier capable of facilitating, independently of the heating effect, the diffusion of the carbon into the mass of the solid steel.

These attempts have already been spoken of briefly in the first part of this volume (see p. 28). Among the patents concerning processes of this kind I shall cite, as example, only the German patent No. 46200, Kl. 48, 1888, and the corresponding English one, No. 9782, 1887, to Robert Kirk Boyle, according to which the iron object to be cemented is connected electrically with the *negative pole* of a generator of current, and at a short distance from its surface, sprinkled with carbon dust, is placed a conductor connected with the *positive pole* of the generator, so that an electric arc may be formed between this conductor and the surface of the steel. To the same group belongs the patent of Georg Mars (German application No. 37948, Abt. VI).

Considerably more numerous are the patents claiming processes of cementation where the electric current is used exclusively as the means of heating. In the patents of this group are described innumerable arrangements, often very complicated, adapted to utilizing in the best way the thermal effects of the electric current. I shall cite only a few, as examples.

Thus, M. Ruthenberg (English patent, No. 19547, 1907) claims the use of a simple electrical resistance furnace, in which the resistor, formed of granular materials or of carbon rods, is separated from the carburizing mass, wood charcoal and barium carbonate.

In the processes described in other patents, such, for example, as those of C. Davis (English patents, Nos. 22233 and 25671, 1901) (in which reference is also made to the heating by means of the electric arc) and of the "Société Anonyme l'Industrie Verrière et ses dérivés" (English patent, No. 5094, 1904), the cementing mass itself acts as the resistor, capable of transforming the electrical energy into heat.

In other patents, finally, are claimed processes in which the resistant mass is composed of the steel objects subjected to the cementation. Among these are the American patent No. 443464 of the "America Spring Co. in Illinois," which is for a continuous process of cementation and of hardening of iron wire; the wire, while it slowly passes through the cementation powder and the hardening bath, is traversed by an electric current sufficient to keep it at the desired temperature.

Very numerous patents claim special types of cementation furnaces, and it would not be possible to give here a complete list of them. Some examples chosen from those based on principles differing markedly from the furnaces



most frequently used in industry have been already described in the preceding chapters.

There are numerous patents concerned with bringing the producer gas, used as cement, directly from the producer to the cementation chamber.

One of the many furnaces of this kind is that protected by the English patent No. 12291, 1901 (Clinch Jones). In it the gas, made in an ordinary producer placed at the lower part of the furnace, issues through two channels, one of which leads a part of it to a combustion chamber, in which it is burnt by air led in through suitable openings, while the other channel leads the remainder of the gas produced into the cementation chamber, heated to the desired temperature by the combustion chamber mentioned above.

The use of ordinary producer gas as cement might, in theory, be justified by the fact that in it carbon monoxide and the hydrocarbons act simultaneously, and we have seen the many advantages which can be obtained by the rational use of these mixtures. But we have also seen that these advantages consist essentially in the possibility of varying at will the concentration and the distribution of the carbon in the cemented zones by means of an *exact* regulation of the ratio between the quantity of carbon monoxide and that of the hydrocarbons contained in the gaseous mixture. It is evident, therefore, that the direct use of ordinary producer gas, for which such an exact regulation is not practically possible, can not give the result mentioned above with the sureness and the precision necessary in practice.

Another problem which various inventors have set themselves, for the purpose of avoiding the very serious disadvantage of the slowness with which heat is propagated from the periphery to the center of the ordinary cementation boxes charged cold, is that of heating separately both the cement and the pieces to be cemented to the temperature of cementation before placing them in contact with each other.

We have already seen how this problem is solved in a very simple and sure way by the processes of cementation, protected by various patents of 1908 and the following years, of the Società Ansaldo & Co. of Genoa, based on the use of mixed cements with carbon and carbon monoxide as base.

For these cements the solution is particularly easy and practical owing to the fact that the solid part of these cements is constituted of the simple "granular" carbon, forming a very mobile mass, especially when hot, which it suffices to "pour" on the objects to be cemented to completely fill the deepest cavities of the most complicated form, and also owing to the fact that the mixed cement, acting preponderantly through the effect of its gaseous constituents, extends its action, with undiminished efficacy, even to the parts of the surface of the steel pieces which are not in immediate contact with the solid carburizing substances. With all the other solid cements, whose efficacy is dependent upon a good contact with all points of the surface of the object to be cemented, the solution of the problem is considerably less simple,

for the operation of the "tamping" of the cement around the steel pieces can not be thought of when the pieces and the cement are heated to redness. And, in fact, we do not find that processes which permit of introducing the charges *completely* heated, employing the usual solid cements, are actually used on an industrial scale.

At any rate, we shall cite, simply as an example, one of the patents claiming a process of this kind; the French patent No. 421961 (October 28, 1910–January 7, 1911), of the "Société des Établissements Partiot." One of the arrangements proposed in this patent consists in using a retort with two arms, arranged at a right angle with respect to each other, both heated in a suitable furnace. In the first phase of the operation, one of the arms of the retort—that placed vertically—contains only the cement, while the other—placed horizontally—contains only the pieces to be cemented. When the cement and the pieces are heated to the temperature adapted to the cementation, the cement is made to pass from the vertical arm of the retort into the horizontal one in such a way as to fill the spaces left free by the steel pieces. The commencement of the cementation is taken as from this moment. In the text of the patent just referred to, it is justly pointed out that one of the chief advantages of cementations carried out by starting with charges completely heated, as compared with those carried out in boxes charged cold, consists in the possibility of computing with exactness the time during which the process of cementation is really effected; this permits of obtaining with precision the desired results.

We might speak here of patents concerning the processes of cementation designed for the manufacture of ship armor, but a discussion of these patents, limited to what is explicitly said in them, would have no interest, because in their specifications, even more than in other patents, the "rule" of giving the least possible exact information useful for the practical application of the processes is closely followed. It would therefore not be possible for me to treat of the "true" content of these patents.

Similar reasons arise from the fact that for some time I have been conducting fruitful experimental investigations in this field at the expense and for the use of others, and so are prevented from giving here an analytical examination of the "*real*" content of the very numerous patents claiming the socalled "metallic cementation," including under this any process which permits of producing the diffusion of elements other than carbon into solid steel.

The great practical importance of the processes of this group has certainly been seen by many of the inventors of cementation mixtures, for many of the patents which claim the invention of carburizing powders or pastes contain additions in which is pointed out how, by adding certain compounds of definite metals (in general, nickel, manganese, chromium, tungsten, etc.) to the carburizing mixtures protected by the patent, the diffusion of those metals



into the solid steel can also be produced, together with the diffusion of the carbon.

We will cite some examples chosen from the many patents containing such an "appendix." One of these is the German patent No. 83093, Kl. 18, 1895 (Francis Gordon Bates), which claims the addition of manganese oxide and of nickel oxide to the carburizing mixture specified in a preceding patent of the same inventor (No. 57729) to produce the diffusion of the two metals into the steel. Another is the German patent, No. 79429, Kl. 18 (Ackermann), which I have already cited. Still another is the French patent No. 327984, 1902, of J. Lecarme, already cited, and from which I wish to take and report here the composition of one of the mixtures recommended to obtain a zone of chromium steel:

| | |
|---|---|
| Fine carbon | 200 grams |
| Water | 1,000 grams |
| Dextrin | 200 grams |
| Pulverized potassium ferrocyanide | 100 grams |
| Potassium chromate | 100 grams |

Other patents also take into account the way in which the heating of the pieces during the cementation is to be carried out. Among these are two German patents, Nos. 211201 and 231971.