

Glasgow and Scottish Section.

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Hon. Treasurer: W. J. Chrystal.

Hon. Local Secretary:

J. Stanley Muir, Chemical Laboratory, University of Glasgow.

Notices of Papers and Communications for the Meetings to be sent to the Local Secretary.

The names in *italics* are those of members of Committee who retire at the end of the current Session.

The following have been elected to fill the vacancies and will take office in July next: *Chairman: G. A. Fawsitt. Vice-Chairman: E. J. Mills. Hon. Secretary and Treasurer: J. Stanley Muir. Committee: G. Bellby, W. J. Chrystal, J. S. Macarthur, T. L. Patterson, E. C. C. Stanford, and G. Watson.*

Meeting held in the Societies' Rooms, 207, Bath Street, Glasgow, on Tuesday, April 5th, 1892.

MR. E. C. C. STANFORD IN THE CHAIR.

THE "DRY HEAT" VULCANISATION OF RUBBER, WITH SPECIAL REFERENCE TO THE USE OF AN IMPROVED VULCANISER.

BY CHARLES A. FAWSITT, F.R.S.E., F.O.S.

FOR the vulcanisation, or as it is technically termed, the "curing" of rubber, four processes are in use, namely, the steam, dry heat, cold cure, and vapour processes.

The "steam" process is used almost exclusively for all goods termed "mechanicals;" and the goods to be cured are packed, either unprotected, or wholly or partially covered, into large iron vessels into which direct steam is turned until the pressure corresponding to the temperature necessary for the proper curing of the goods is reached, and is continued for a time, which varies according to quality, thickness, &c., of the goods. The "dry heat," "cold cure," and "vapour" processes, are principally used in the curing of waterproof cloth.

The "dry heat" consists in mixing the rubber with a small percentage of sulphur and other ingredients, and "curing" the cloth spread with such a mixture in a stove or air chamber heated by pipes or chambers through which steam or hot air circulates.

The "cold cure" process consists in exposing the rubber composition which has been spread on the cloth to the action of chloride of sulphur dissolved in bisulphide of carbon or other solvent.

The "vapour" process consists in exposing the goods which are to be cured to the action of the vapour of chloride of sulphur alone or mixed with nitric acid in large chambers, or merely by passing the proofed side of waterproof cloth over vessels in which the same reagent is slowly evaporated.

I shall, in what remains of this paper, treat almost exclusively of the curing of waterproof cloth, or, more correctly speaking, of the film of rubber which renders the cloth waterproof.

At present there is a revolution taking place in the rubber trade, so far as the vulcanisation of waterproof cloth

is concerned, in favour of the "dry heat" versus the "cold cure" process; and, considering the usual disinclination of manufacturers to depart from old methods, it has come with extraordinary suddenness, so much so, that it has caused consternation amongst the manufacturers of bisulphide of carbon and chloride of sulphur, whose business will suffer very severely unless new outlets are discovered for their products.

Until within the last two years the majority of rubber manufacturers used the "cold cure" process almost exclusively for the production of single and, to a considerable extent, in that of double texture waterproof garments, and as it was a process which had been gradually developing and increasing for years, its discontinuance was all the more surprising.

In Scotland the manufacturers have all adopted the "dry heat" process, but in England matters have not so far advanced in this direction, as some of the leading firms still cling to the "cold cure" as the safest and best process, but no doubt they will be forced to partially adopt it, as "dry heat" goods are now specially asked for.

The "dry heat" process has been very largely and successfully applied in America, and I think the Americans are to be congratulated as the first to thoroughly work it out, and it is mainly through their experience that manufacturers have been persuaded to adopt it in this country.

Perhaps, before we proceed further, it would be as well to look at the reasons which have brought about this change of front on the part of rubber manufacturers; and I think this can best be done by stating in a few words the advantages and disadvantages of each process. The advantages of the "cold cure" process were:—1st. The production of what is called a "transparent" proofing, which was and still is, though perhaps in a lesser degree, prized for single texture garments. 2ndly. The speed and cheapness of the process compared with the "dry heat." What I mean by cheapness here has nothing to do with the composition of the proofing, merely the cost for curing. 3rdly. The non-efflorescence of cold-cured goods, which is of much importance, and the reason of which has not been satisfactorily explained. Digressing for a moment, I shall mention one or two points in connexion with efflorescence which may be of interest. How is it that in cold-cured rubber we can have, say, 9 per cent. of sulphur present without efflorescence, when in the "dry heat" process 3 per cent. is dangerous? Some may say it is accounted for by the rubber never having been heated above the melting point of sulphur, but I tested this idea by heating pieces of cold-cured rubber containing more than 6 per cent. of sulphur above its melting point, but found no efflorescence. The following may be a possible explanation:—Some time ago a paper was read before the British Association by Thomson (1890, p. 785), in which he stated that when rubber was cold-cured it contained not only sulphur, but chlorine, the latter element being almost invariably double of the former. Now it occurred to me that the non-efflorescence of cold-cured might be accounted for by the sulphur and chlorine existing together in the rubber in combination.

Of course it might be advanced as a reason against such a theory that the greater part of the sulphur can be extracted with bisulphide of carbon, which fact I mentioned in a paper read before this Society (Jour. Soc. Chem. Ind. 1889, 368), but although such is the case, may not the chlorine be extracted at the same time and which would no doubt be the case if it existed as a compound. I am sorry at not having proved or disproved this idea, but want of time has prevented me.

Now, as regards the disadvantages of the cold-cure process:—

1st. The chief cause which led manufacturers to embrace the "dry heat" process, was the loss occasioned by damaged goods when using the cold-cure process, and the damage often arose from causes which, apparently, could not be explained. The blame was usually put upon the oil contained in cloth, but I think this was only occasionally the real cause, and my sympathy was often on the side of the cloth manufacturers, who usually, rather than lose a customer, paid the claim put upon them. No doubt

manufacturers often made mixings which were very unsuited for this process, but naturally preferred to throw the blame on other shoulders.

2dly. The injurious action of the vapour of bisulphide of carbon on the workmen employed in attending to the "curing" machines. In some works this is reduced to a minimum and is not urged as an objection, but it is not the case in the majority of manufactories.

3dly. It is put forward by the majority of firms that cold-cured goods do not stand hot or cold climates so well as could be desired, the strong light combined with the heat and perspiration from the body, exerting a powerful decomposing action in hot climates. The light is, I think, the chief agent in bringing about the mischief.

4thly. It is not possible to adulterate the rubber so easily when using chloride of sulphur as the curing agent, which in these days of low prices is of great importance.

My experience so far has been that a piece of rubber cold-cured properly, is the most perfectly vulcanised of any made, but the conditions which ensure say of a piece of sheet being so cured, are perhaps not possible in the case of proofed cloth, at any rate not easily attainable.

The advantages of the "dry heat" process are mostly implied by the disadvantages of the cold-cure process just mentioned, for—1stly. There is comparatively little claim for damaged goods, and cloths can be used containing a proportion of oil which would be inadmissible in the cold-cure process. Now, although the damage arising from the action of the cloth on the proofing is in the dry heat much reduced, yet it must not be inferred that it is entirely absent, as it is noticed with poor quality of black and brown cotton cloths that 12 months is about sufficient to cause the decomposition of good proofing. This is due to the mordants and dyes used. 2dly. The use of bisulphide of carbon is avoided. 3dly. The proofing is said to stand extreme heat and cold better than that made by the cold cure. 4thly. A cheap proofing can be worked.

As regards the disadvantages of dry-heat process, we have—

Firstly. The danger from efflorescence which has been the chief cause of complaint against manufacturers; and as black paramattas are coming more into fashion, this is a point of much importance.

Secondly. The large amount of stove space required to turn out a large quantity of waterproof cloth.

Thirdly. The cost per yard for curing is double that of the cold cure; no doubt this is made up for by being able to use a cheaper proofing, but it is a point in favour of the older process.

Fourthly. The non-possibility of producing "transparent" proofing which is distinguished from ordinary "dry heat" proofing by its softness and elasticity as well as its transparency.

It may be asked why not use the "steam" process for curing waterproof cloth when it is used for other goods; and the answer is that although it would cure the rubber well and with less danger of efflorescence than with "dry heat," yet it is fatal to the colours of the cloth and also to the cloth itself. Before the "dry heat" process came in, it was used, but never to a large extent except for black and white sheeting.

What is the "bon ideal" of a vulcanised process for waterproof cloth? This question is difficult to answer satisfactorily, but I should say it would be fulfilled by a process which in the shortest time and at the lowest temperature, consistent with a sound vulcanisation, would produce a proofing which would stand the hottest and coldest climates, and not effloresce, and at the same time could without unusual difficulties be produced at a cost which would enable manufacturers to use it even for cheap goods.

When manufacturers who had been accustomed to work with steam and cold-cure processes began to face the "dry heat" process, a few difficulties presented themselves, which were not easily overcome. For instance, if you take a piece of rubber mixed with 4 per cent. of sulphur, and heat to 250° F. in a "dry heat" stove, it becomes soft and unfit for use, but if the same piece were steam-heated it would cure up satisfactorily. To overcome this, quite a different

class of mixings had to be arranged to satisfy each quality of proofing. Again, the difficulty of avoiding efflorescence and at the same time get a satisfactory vulcanisation caused considerable trouble, and the experience was often gained through the loss of custom, because time is the factor which tells most forcibly as a test on rubber goods. Again, buyers who had been accustomed to purchase the finely-finished transparent garments with a velvety feel, and good elasticity did not readily take to single texture goods with dark proofing, and not so soft to the touch and with less elasticity. Of course, for light cloths it is not of great importance to avoid efflorescence, but for black or dark cloths it is necessary to avoid it completely. This efflorescence could be avoided by using a high temperature or a long-continued heat, but then the cloth suffered. In fact woollen cloth is found to "tender" slightly at 240° F., hence the importance of using a low heat and short time, both being consistent of course with a sound proofing. With ordinary "dry heat" proofing we cannot look for a lower temperature than 238° F., as sulphur melts at that heat; and anything below this is of no use; hence the obvious necessity of bringing up the heat of the stove as quickly as possible to this temperature. As regards the duration of the heat, it altogether depends on the composition of the proofing, but, as a rule, however, for good proofing 1—2 hours at 240°—245° F. reckoned from the time the temperature reaches 240° F. is about what is required.

The management and construction of the stoves requires considerable practical knowledge. Steam at 10 lb. pressure would be more than sufficient to produce a temperature of 238° F., assuming that no heat was lost by radiation and convection, but for large stoves nothing less than 60 lb. is used, and it is more economical to work with a still higher pressure, as the heat can be brought up more quickly to the melting point of sulphur, and so more work can be got out the stove in a given time.

About two years ago my firm was asked for a vulcaniser which would be suitable for the production of transparent proofing by the "dry heat" process, and as I thought such a thing quite feasible I had a series of trials conducted, which resulted in the production of a vulcaniser which answered the purpose, and has been found to be useful, not only for that special class of work, but also for other purposes which had not been anticipated. After completing the laboratory trials, the North British Rubber Company, who have had the longest experience in the "dry heat" process of any firm in Great Britain, kindly undertook the practical trials, and under the superintendence of Mr. A. Douglas have, during 1891, carried them to a successful issue, in so far that they have proved it suitable for the production of "transparent" proofing, and also have introduced it into the manufacture of other goods, such as fishing stockings.

Through their kindness, I am able to show you to-night samples of some of the goods which they are now producing, and the more important of which are the pair of fishing trousers which Mr. Douglas got made for his own use last October, and, although they have been in use since that time, are in very good order; also a new pair of fishing stockings, which show very well the nature of the proofing. The colour you will notice is odd, and can no doubt be improved, but what is wanted in these goods is a good tough proofing, irrespective of appearance. I am informed, moreover, that these stockings if damaged can be repaired, which is a special property. We have also two samples of transparent proofing, which serve to show the results which can be obtained in this direction.

I had hoped Mr. Douglas would have been present to-night to explain the chief points of difference between these sample goods and those made by other processes, but as he was prevented from coming he wrote to me, and, after giving a list of the articles, he goes on to say, "The fishing goods are spread with pure gumi, with 4 per cent. of patent vulcaniser. They are heated for two hours, 50 minutes of that time being at 240° F. The rubber is exceedingly tough, more so than it would be by any other process, and the short and low temperature reduce the risk of tendering the fabric very considerably."

The two "transparent" samples are spread with the same gum as the fishing stockings. The silk one was spread July 1891, and vulcanised three-quarters of an hour at 240° F.; whilst the union silk was spread last week, and heated one hour 240° F. This gum, more particularly in very light spread goods, has a very soft and agreeable feel, and looks well, but I am afraid the high prices of your patent vulcaniser will seriously interfere with its adoption by manufacturers for the single texture waterproof garment trade, which is to be regretted, as I consider it the best form of vulcanisation at present known for these goods."

I have here also samples of coloured sheet-rubber, kindly prepared for me by Messrs. W. Warne & Co., which contain only 2 per cent. of vulcaniser. The vulcanisers used in these trials were the iodides of the heavy metals mixed with sulphur.

In my patent I claim all iodine and bromine compounds, but, so far, have found those of the heavy metals to give the best results. The addition of sulphur was found to be necessary, as without it it was impossible to obtain good results.

The points which were forcibly brought out during the trials were:—1st. The very small percentage of compound which was necessary to ensure complete vulcanisation. The iodide could be reduced to 1½ per cent., whilst the sulphur was 2 per cent., and you can well understand that 3½ per cent. of compound would not affect, to any extent, the transparency of the rubber. 2ndly. The low heat required for complete vulcanisation. This seems a very important point, as most manufacturers experience great difficulty in getting a satisfactory "cure" at a temperature which does not injure the cloth. The extreme sensitiveness of the vulcaniser to heat caused a little trouble at the commencement of the trials, as they were conducted too much on the lines of the ordinary "dry heat" mixings. I remember the first trials which were made had as much as 15 per cent. of the iodide and 6 per cent. of sulphur, and the astonishing thing was, that these samples cured at 200°–205° F., considerably below the melting point of sulphur, which was very unusual, and proves that whatever action takes place it does so in a manner quite different from the ordinary process in which no action is apparent below 238° F., although a considerable proportion of the "curing" agent is present. Of course when using such a high percentage of the vulcaniser you can naturally imagine that a large proportion remains unexhausted, and is ready to still further affect the rubber. This was proved by heating a piece of such rubber to 240°–245° F. for but 39 minutes, when it became quite hard. The property possessed by this vulcanizer of exerting a curative effect considerably below 238° F., although of little practical importance at present, may at some future time receive useful application. 3rdly. The quickness of the cure was rather surprising, as one half hour was sufficient when using 3 per cent. vulcaniser and 2 per cent. sulphur, and when using a high percentage along with a high temperature the "cure" was effected in a few minutes. With 15 per cent. ten minutes at 250° F. would suffice.

A quick cure is regarded by some rubber authorities with suspicion, and, I think, naturally, as the ordinary method employed, and which must force itself upon the mind for comparison, does not cure under two hours at 238° F. I found that with this new compound it was safest to use a small percentage and lengthen the heat, but an hour seemed sufficient for all ordinary purposes, using say 2–3 per cent. with 2 per cent. of sulphur. With these proportions the curing agent seems to be exhausted after one hour's heating. To prove this, a piece of mixed rubber was cut into two pieces; one was heated for one hour at 240° F., and the other for five hours, when they were both equally cured, showing that with the extra three and a half hours heating no further effect was produced. The fact of the vulcaniser curing so quickly and at such a low temperature is a saving, in that more work can be got out of a stove in a given time, which is of considerable advantage in the "dry heat," as large stoves are required to put through a large quantity of cloth.

The continuous stove patented by Waddington, and worked by Messrs. Charles Macintosh & Co. and others, through which the cloth is slowly drawn, ascending and descending many times before it is finally wound upon a roller on the outside, seems to be a move in the right direction, as by this system the cloth can be tested occasionally, and the speed of the rollers regulated according as to whether the proofing is over- or under-cured; it also prevents the creasing and marking of the proofing, which is a common occurrence in ordinary stoves. This system of curing would be specially applicable when using this new vulcaniser, seeing it is more sensitive to heat than that used for ordinary work.

Whilst working with this vulcaniser a difficulty presented itself which caused some trouble, although a simple remedy was found to obviate it. When working with woollen and almost all kinds of union tweeds, the proofing cured up quite satisfactorily, but when working with cotton cloths containing black and brown dyed yarn the proofing became tacky and refused to cure quite satisfactorily. It was very noticeable with, say, a piece of black and white check cotton cloth, because wherever the proofing was upon the black squares it was soft and under-cured, but upon the white squares it was quite cured, and in every respect satisfactorily. Seeing that black woollen cloth was free from this peculiar action, it could only be caused by the different manner in which the dyes were fixed in the two cases. In the case of the cotton, the mordanting material was thought either alone or in combination with the dyestuff to cause the mischief. It being difficult to tell what colours were to blame in cloths containing many colours, I procured cotton-dyed yarn of different colours, and got them knitted into strips, which were then spread with rubber dough containing a proportion of vulcaniser which was known to be more than sufficient to cure it. After curing for two hours at 240°–245° F., the proofing on the white, blues, drabs, and certain shades of brown was quite vulcanised, but on the black and dark browns it was under-cured.

As the black cloth had caused the most trouble, attention was specially directed to it, to find out, if possible, the cause of this action. In the first place the opinion of an experienced dyer was taken as to the probable process used in dyeing the yarn. After a critical examination he reported that the mordant was iron liquor, the "prepared" tannin, and the dye logwood. Three pieces of white cotton cloth were next taken, and after well scouring and drying treated as follows:—

No. 1	soaked in a solution of iron liquor.
" 2	" " " tannic acid.
" 3	" " " logwood.

They were now dried and spread with rubber dough of same composition as that previously used. After drying they were cured two hours at about 240° F., and it was found that in each case the proofing was sound, so separately the reagents did not interfere with the curing. Next, three pieces of cloth were taken, scoured, and treated as follows:—

No. 1	dipped iron liquor, afterwards tannic acid.
" 2	" " " logwood extract.
" 3	" " " then tannic acid, then logwood extract.

After drying they were spread with rubber dough and cured as before, when No. 1 cured, but not Nos. 2 and 3, proving apparently that it was the compound produced between iron oxide and colouring matter of the logwood which accounted for the mischief. Want of time prevented me from going further into the matter, and trying if possible to find what the cause of this action was, i.e., how could this dye compound so influence the iodide or the mixture of iodide and sulphur as to retard its curative action. It almost looked as if the dye compound so affected or combined with the sulphur as to render it less available for the iodide, as the addition of extra sulphur was found to be an antidote as regards the curing, but was inadmissible when working with black cloth because of danger from efflorescence. It was suggested, as a probable explanation, that the tweed cloths which are usually sold might contain some of the

mordant unwashed out, or greasy matter, so pieces of such cloths, containing a good admixture of black and brown were treated as follows:—

No. 1.—Treated three times with ether, to remove grease.

No. 2.—Boiled three times in water.

No. 3.—Boiled weak acid, then water.

No. 4.—Boiled weak alkali, then water.

After drying they were spread and cured two hours 240° F., but the proofing was useless, which disproved the theory of grease or mordanting material being left in the cloth.

It has long been known that copper and certain of its compounds exert a deleterious effect on rubber, and this was brought forward lately by Thomson (*India-rubber Journal*, 1891, 328), but in the above examples copper was absent.

I asked Mr. Christie, of Messrs. J. Orr Ewing & Co., who has had a large experience in the dyeing of cotton yarn, if he could offer an explanation, and he thought the reason might be the presence of peroxide of iron, and suggested the procuring of a piece of buff cotton cloth, much used for window-blinds, and which, he said, would be free from all foreign matter, such as tannic acid and logwood, used in dyeing black and brown yarn. I did this, and found that the action of the vulcaniser was retarded, almost proving that the iron oxide was the cause of the mischief; but if this were proved, the next question would be, what is the reaction which takes place? Although this action was peculiar, and, in the meantime, to me inexplicable, yet a simple remedy was found to allow of its being used on cotton cloths. This consisted, in the first place, in giving the cloth a coat of pure rubber dough, mixed with 2 per cent. of sulphur, and which is often resorted to in ordinary "dry heat" process to avoid "efflorescence."

The action of dyed cloth on rubber proofing is an important question, not only for the rubber manufacturers but also for dyers, and it seems to me that the solving of the problem should not be left to manufacturers, but to the dyeing schools, who, so far as I know, have given the matter little or no attention, and some of the wealthy rubber manufacturers could, with advantage, encourage the investigation of such questions in the technical schools.

An important point in connexion with the use of this new vulcaniser is, that by its means coloured rubber proofing can be easily obtained without adding a large amount of pigment to the rubber. In the ordinary "dry heat" process it is difficult to get a good coloured "proofing," and at the same time keep the proportion of compound so low that it will be elastic.

With this vulcaniser, however, brown, drab, red, blue, and green proofings can be obtained.

I have here a few samples of coloured proofings which Messrs. Campbell, Achnach, & Co., kindly prepared for me, and you can judge better of their appearance and softness to the touch by inspection.

Of course, if wanted, the pigment can be increased, as I have had 360 per cent. added, as per sample shown, and still the rubber was strong and elastic.

The coloured proofings cured up in a time according to the percentage of vulcaniser and compounding material added, but the usual time was three-quarters of an hour at 240°–245° F.

It mixes very well with most pigments, but there are some which retard its action. It appears to me that proofing cured with it could be finished without farina, as the surface after curing is very dry and soft, and, if so, it would be a point in its favour, as farina seems to exert a deleterious action on the surface of the rubber, (no doubt through its getting damp and fermenting; besides, farina comes off when wet upon the cloths, and leaves marks, which is objectionable).

Two most important questions in regard to the introduction of this new vulcaniser are, as to its keeping qualities and its cost.

Firstly. As regards its durability, it is impossible to give an answer based on long experience; but when one takes into account the fact that the samples which were made in the preliminary trials 15 months ago are still in good condition, it is surprising, as too much vulcaniser was

used, and the method of working has been much improved. There can be no question, I think, that the "transparent" dry-heat proofing will stand better than that cold-cured in warm climates. To test their heat-resisting properties, a piece of each of these kinds of proofing, and also a piece of that which had been cured by ordinary "dry-heat" process were taken and heated to 300° F. for half an hour. The cold-cured piece was simply rotted away; the ordinary dry-heated piece had quite decomposed, whilst that cured by the new vulcaniser was but slightly so, showing that it was not readily affected by heat. Judging from my own experience, and the interchange of opinion I have had with Mr. Douglas and others, I conclude that there is every probability that the rubber will keep as well as the ordinary "dry heat" rubber.

Secondly, as regards the cost. At first sight it would appear as if the cost would be such as to preclude it from general use, but on looking more closely into the question it wears a different aspect. Taking the average weight of "transparent" proofing on a coat at 2 lb., we have for this weight 4d. worth of vulcaniser. Now there falls to be deducted from this the cost of curing by the ordinary method, which is about one penny, and we must also take into account that by the rapid curing a considerable saving is effected, so the difference in price is certainly not prohibitive. If it is compounded, of course the price can be reduced to that of ordinary curing.

It may be asked, will this compound mix with rubber substitutes, and I may say that the ordinary oil substitute made with chloride of sulphur is quite as unsuitable as it is for all "dry heat" work. Oil vulcanised with sulphur by heat is suitable, but the admixture of different substances is one which only can be determined by the manufacturers themselves.

The cheapening of rubber by adding different foreign materials has become quite an art, and a necessary one, no doubt, and something will soon be found which will serve as an article to cheapen the mixing with the new compound also. It has been tried for double as well as single texture garments, and is very serviceable where a nice pliable proofing is wanted and when a cloth is being dealt with which is easily affected by heat.

It is principally in connexion with "dry heat" that it has been tried, but it gives good results in the steam heater when wrapped up to protect it partially from the steam. I have here a piece of sheet rubber cured 2½ hours at 260° F., which shows that by this process it is possible to bring about good vulcanisation, as the rubber, you will notice, is very strong.

My best thanks are due to Mr. Anderson, who conducted all the experimental work involved in testing the properties of this new vulcaniser; and also to Mr. Douglas, Mr. Burbridge, and Mr. Cairns, for their kindness in preparing samples and giving valuable advice.

DISCUSSION.

The CHAIRMAN said that he thought it would be difficult to exaggerate the value of this paper. Mr. Fawsitt seemed to have made a remarkable discovery in the vulcanisation of rubber. He should like to ask what particular iodide he used.

Mr. J. W. BIGGART said that Mr. Fawsitt remarked that light seemed to have an injurious effect upon the rubber, as instanced in the case of the goods hanging in a shop window. This seemed to indicate that a chemical change took place under the influence of light, and he should like to ask what change it was that actually did take place.

Mr. FAWSIFF, in reply to the Chairman, said that the iodide used in all the trials for the fishing stockings and other specimens shown was iodide of antimony. They fixed on that in preference to iodide of tin because antimony was a cheap material and produced good results; iodide of tin also gave good results; but seeing they had commenced with antimony, they did not wish to alter meantime. Regarding the reaction which took

place in the vulcanisation, he had never formed a satisfactory opinion on that point, as they had not had time to go into the subject fully.

With reference to the question asked by Mr. Biggart as to the effect of the rays of the sun on the proofing, he could not give particulars of the chemical change that took place.

ON THE COMPOSITION OF "HUNYADI JANOS" MINERAL WATERS.

BY J. W. BIGGART.

THAT the mineral waters as a class occupy a very important place in *Materia Medica* is an acknowledged fact. Regarding the properties of many of them there is a common belief that to the waters as found in nature belong qualities which art cannot reproduce by any of its preparations or imitations. Many medical men hold this opinion, and for obvious reasons it is a notion suggested and encouraged by all those who have a proprietary interest in any of the wells.

While it is here granted that the artificial waters must and will differ in properties from the natural, if any of the various radicles in the artificial imitations be brought together either in a different order or in different amounts from that which they hold in the natural water, still it is hard to see, how, if these combinations and the gases present in the water be exactly known and the data deduced from them correctly followed, there can or will be any difference between the medicinal qualities of a natural water and its artificial imitation. In short, if the salts present and their amounts be known then the water can surely be prepared. It is on one of these natural mineral waters called "Hunyadi Janos," that this short note and analysis have been prepared, and it may be of some interest to state that it is one of the most popular aperient waters having a sale which is reckoned by several million bottles per annum.

Concerning this water, the writer has heard it repeatedly stated (by medical men) that it possesses properties so peculiarly its own that they cannot be reproduced by art, but, discrediting such a theory, its analysis and examination were undertaken.

The generally accepted opinion concerning the composition of the water is that it contains principally magnesia and sodic sulphates and chlorine combined with sodium as common salt.

For the most part this opinion has been verified, but in one respect, namely, the state of combination of the chlorine, a vital and important difference has been observed, as shall be presently pointed out.

The analysis of the salts left on evaporating a portion of the water gave the following percentages of the different radicles:—

Basic.		Acid.	
Soda	1.00	Silica	Trace.
Magnesia	0.535	Sulphuric acid....	2.42
Lime	0.18	Chlorine	0.101
Iron	Trace.	Phosphoric acid...	Trace.

On looking over these results it is apparent that all the lime must first be calculated to sulphate. After this it is necessary to discover to what base or bases the chlorine is linked. Then it only remains to calculate soda and magnesia left to sulphates. As the condition of the chlorine is the only point which presents any difficulty, the particular state of its combination was arrived at in the following manner:—A measured volume (50 cc.) of the mineral

water was evaporated spontaneously in the air (this precaution was adopted to ensure against any double decomposition taking place between the salts).

After evaporation the salts were taken up with absolute alcohol, which dissolved the chlorides present, but left the sulphates as an insoluble residue. The alcoholic extract was next evaporated to dryness (also in the air) and the residual mass taken up as before. The acids and bases present in this solution were then estimated, and they were found to be practically pure magnesia chloride. Proceeding on these data, and linking the proper bases to their own acids, calculation showed the composition of the water to be as follows:—

	Parts per 1,000.
Calcic sulphate.....	0.41
Magnesia do.	16.65
Sodic do.	25.00
Magnesia chloride.....	1.20
Silica	0.12
Water.....	957.22
	<hr/> 1,000.00

DISCUSSION.

The CHAIRMAN said that the composition of these mineral waters was extremely interesting, and the one which was the subject of this paper was perhaps the most interesting of all. It seemed that waters the same as this and to have the same effect could be artificially made. It was well known that for many years there was a German spa at Brighton, where the waters made were an exact imitation of many of the German natural waters. He had used Hunyadi Janos water in his own house for many years, but had always prepared it himself, and never could find any difference from the natural water. He knew that the composition of the artificial water was always the same, and the natural water was not. He should like to ask if Mr. Biggart found no potash salts in this water, as he understood that there was always small quantities of sulphate of potash and of bicarbonate of soda present?

Mr. T. L. PATTERSON did not think that Mr. Biggart's method of analysis proved conclusively the presence of magnesium chloride in Hunyadi Janos water, as there was no doubt that chemical changes might take place on addition of absolute alcohol to the mixture of salts, resulting in the formation of easily soluble magnesium chloride.

Dr. G. G. HENDERSON agreed with Mr. Patterson in thinking that Mr. Biggart's analysis left it doubtful whether magnesium chloride was present in the natural water. He should like to know whether the dissolved gases had been estimated. He thought there was a large field open to manufacturers of mineral waters, for it would be quite unnecessary in many cases to go to German spas, or to buy the foreign mineral waters imported into this country in such enormous quantities, if these waters could be prepared artificially at home. There ought to be little difficulty about this, seeing that the composition of most of the waters was well known.

Mr. BIGGART, in reply to the Chairman, said that he had examined the residue for potash salts, but had failed to detect them. He had not estimated the dissolved gases.