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what I have stated in this letter will probably be just as "erroneous" in Mr. Keith's views, that is, just as conformable to the opinion of all mathematicians who are competent judges, as my various statements in the critique inserted in your Magazine for November.

I am, sir, yours, &c.

*The Reviewer of Bonycastle's Trigonometry.*

February 12th, 1807.

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XI. *A third Series of Experiments on an artificial Substance, which possesses the principal characteristic Properties of Tannin; with some Remarks on Coal.* By Charles Hatchett, Esq. F. R. S.\*

§ I.

IN my former papers upon this subject, some account has been given of the effects produced by sulphuric acid upon turpentine, resin, and camphor; and I shall now state the results of other experiments made with the same acid upon a great number of the resins, balsams, gum resins, and gums, the greater part of which afforded that modification of the artificial tanning substance, which, for the sake of distinction, I have in the preceding papers denominated the third variety.

The process was simple digestion in sulphuric acid, after which, the residuum was welledulcorated, and was then digested in alcohol. This was separated by distillation, the dry substance which remained was infused in cold distilled water, and the portion dissolved was examined by solution of isinglass, muriate of tin, acetite of lead, and sulphate of iron.

Much sulphureous acid, carbonic acid, several of the vegetable acids, particularly benzoic acid, (when the balsams were employed,) and apparently water, were produced during the operation; but in this paper I shall only notice two of the products, namely, the tanning substance and the coal.

\* From the *Transactions of the Royal Society for 1806.*

The sulphuric acid almost immediately dissolved the resins, and formed transparent brown solutions, which progressively became black.

The same effect was produced on most of the other substances, but the solutions of the balsams and of guaiacum were at first of a deep crimson, slightly inclining to brown.

Caoutchouc and elastic bitumen were not dissolved, but, after having been digested for more than two months, were only superficially carbonized.

The gums and the saccharine substances required many evaporations and filtrations before the whole of their carbonaceous residua could be obtained.

These were the principal effects observed during the experiments, and I have stated them in this manner, that tedious and useless repetitions may be avoided.

## § II.

Turpentine, common resin, elemi, tacamahac, mastich, copaiba, copal, camphor, benzoin, balsam of Tolu, balsam of Peru, asa foetida, and amber, yielded an abundance of the tanning substance.

Oil of turpentine also afforded much of it; asphaltum yielded a small portion; some slight traces of it were even obtained from gum arabic and tragacanth; but none was produced by guaiacum, dragon's blood, myrrh, gum ammoniac, olibanum, gamboge, caoutchouc, elastic bitumen, liquorice, and manna. I am persuaded, however, that many of these would have afforded the tanning substance had not the digestion been of too long a duration.

Olive oil was partly converted into the above-mentioned substance, and also linseed oil, wax, and animal fat; but the three last appear to merit some attention.

### *Linseed Oil.*

This oil with sulphuric acid very soon formed a thick blackish-brown liquid, which, after being long digested in a sand-bath, was still partly soluble in cold water, and passed the filter. This solution precipitated gelatine; the residuum was a tough black substance, which became hard on exposure to air. A great part was soluble in alcohol, and formed

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a brown liquid, which became turbid by the addition of water. When this was evaporated, a brown substance remained, which was partially dissolved by cold water, and the solution thus formed was rendered turbid by gelatine.

The undissolved portion left by the alcohol was of a blackish-brown; it was soft and tenacious, and appeared to retain many of the properties of an inspissated fat oil.

*Bleached Wax.*

That which was employed in this experiment was the white wax of the shops, which is sold in the form of small round cakes. It formed with sulphuric acid a thick black magma, and was not acted upon by cold distilled water when washed with it upon a filter. Upon being digested with alcohol in a sand-bath, a brownish solution was formed, which upon cooling became very turbid, and appeared as if filled with a white flocculent substance. The same operation was repeated with different portions of alcohol until this ceased to act. The whole of the solutions in alcohol were then mixed, a large quantity of distilled water was added, and the alcohol was separated by distillation.

On the surface of the remaining liquor, when cold, a white crust was formed, which being separated was found to possess the properties of spermaceti, and weighed 18 grains. The filtrated liquor was then evaporated to a small quantity, became of a pale brown colour, and was rendered turbid by solution of isinglass.

*Animal Fat.*

This experiment was made upon the kidney fat of veal, but I cannot take upon me to assert that the results would have been the same with every kind of fat. 100 grains of it with one ounce of concentrated sulphuric acid, after some time, formed a blackish soft mass; a second ounce of sulphuric acid was then added, and the whole was digested and occasionally heated during nearly three months. Six ounces of distilled water were poured upon the black pulpy mass, and formed a thick uniform liquid, which, after digestion for six or seven days, was when cold filtrated. The liquor which passed was of a brown colour, and upon evaporation

poration became black, leaving a considerable portion of a blackish substance upon the filter, which was added to that which had been collected by the first filtration. The whole was washed with cold water, which passed colourless. Boiling water was then poured upon the filter, by which a considerable portion was rapidly dissolved, and a brownish-black solution was formed, which copiously precipitated gelatine.

The residuum on the filter was then dried, and being collected was digested in alcohol, which dissolved the greater part.

The solution in alcohol was filtrated, but (apparently by the effect of air) a considerable deposit was formed on the filter, which was again dissolved by alcohol. Water rendered the solution turbid, and a black light flaky substance, which weighed 41 grains, remained upon the filter. The filtrated liquor was then evaporated, and left a grayish-black substance, which weighed 30 grains. This last substance was highly inflammable, and when burned emitted a very peculiar odour, resembling partly that of fat and partly that of asphaltum. It easily melted, and also immediately dissolved in cold alcohol, from which, like the resinous substances, it was precipitated by water.

The black light flaky residuum, which weighed 41 grains, was found to consist partly of the substance above mentioned and partly of coal, but the proportion of this last was not ascertained.

Coagulated albumen and prepared muscular fibre were also separately exposed to the action of sulphuric acid in the manner above described, but did not afford any substance by which gelatine could be precipitated, coal being the only product which remained.

Almost every one of the bodies which have been employed in these experiments, seem to be in some measure different in respect to the progressive effects produced upon them by sulphuric acid; and all other circumstances being similar, there appears to be a certain period of the process when the production of the tanning substance has arrived at its maximum, after which, a gradual diminution of it takes place,

and at length total destruction. These effects are produced at different periods, according to the substance which may be the subject of the experiment, and therefore it is impossible at present to state the utmost quantity of the tanning substance which, under equal circumstances, may be obtained from each of the resins, balsams, &c.

The tanning substance appears to be always the same, whether obtained from turpentine, or common resin, or from the balsams, or from *asa fœtida*, or camphor, or indeed from any of the bodies which have been enumerated; its effects on the different reagents are similar; by the addition of a small portion of nitric acid, and subsequent evaporation, it is converted into that which I have called the first variety; or if digested with sulphuric acid, it is speedily destroyed, and becomes mere coal. In the latter case, therefore, the same agent which at first produced it becomes at length the cause of its destruction; and thus we find that although a tanning substance may be obtained from resinous and other bodies by means of sulphuric and by nitric acid, yet in the former case the product is variable, and is formed at or about the mean period of the operation, whilst the latter is an ultimate and invariable effect, beyond which no apparent change can be produced by any continuation of the process\*.

### § III.

I have already stated, that caoutchouc, and elastic bitumen, were only superficially acted upon when digested for a very long time in sulphuric acid; and it is remarkable, that these substances, which in their external characters so much resemble each other, should be similar in their habits when exposed to the effects of this acid; for, unlike the resins and most of the other bodies which were subjected to the preceding experiments, and which were almost immediately dissolved when the acid was poured upon them, these on the contrary remained undissolved, and only became partially carbonized on their surfaces. Even nitric acid does

\* In the former papers upon this subject I have observed, that the tanning substance produced by sulphuric acid is very inferior in energy to that which is formed by nitric acid.

not so rapidly effect a change in the elastic bitumen as it does when applied to the other bituminous substances.

1. 100 grains of pure soft elastic bitumen were digested during three weeks in one ounce of nitric acid, diluted with an equal quantity of water; a tough and slightly elastic orange-coloured mass then remained. Another ounce of the acid, not diluted, was poured upon this mass, and the digestion was continued until the whole was evaporated. The residuum was tenacious, and of the colour above mentioned. Water partially dissolved it, and formed a deep yellow liquid, which copiously precipitated gelatine, and possessed the other properties of the tanning substance which is produced from the resins, &c. by nitric acid.

An orange-coloured mass still remained, which was speedily dissolved by alcohol, and was precipitated from it by a large addition of water.

This substance in many of its properties resembled the resins, but in others, seemed to approach those which characterize the vegetable extractive matter. It appeared to be similar to that which has been cursorily mentioned in my first paper, and which was obtained from many of the pit-coals and bitumens when treated with nitric acid. I have since paid more attention to this substance during the following experiments :

Kilkenny coal was digested with nitric acid, and progressively, although with difficulty, was converted into that variety of the tanning substance which has so often been mentioned. Similar experiments were made on the same sort of coal from Wales, which was given to me by my friend Mr. Tennant, as well as upon a coal sent to me by Professor Woodhouse, which was from Pennsylvania, and is there called Leigh high coal. All of these were converted into the tanning substance, but they did not yield any product similar to that obtained from the elastic bitumen.

The contrary, however, happened when the common pit-coal, or Cannel coal, or asphaltum, were employed. For when these were treated in the way which has been described, and when the digestion was not too long continued, then I obtained from 100 grains of each of the above sub-

stances (after the separation of the tanning matter) a residuum as follows :

From 100 grains of the common Newcastle coal 9 grains.

From 100 grains of Cannel coal - - 36 grains.

From 100 grains of pure asphaltum - - 37 grains.

The substances thus obtained were very similar in their external characters, being of a pale brown, approaching to Spanish snuff colour ; their internal fracture was dark brown, with a considerable degree of resinous lustre. When exposed to heat they did not easily melt, but as soon as inflamed they emitted a resinous odour mixed with that of fat oil, and produced a very light coal, much exceeding the bulk of the original substance.

Alcohol completely dissolved them, and if water in a large proportion was added to a saturated solution, a precipitate was obtained ; but after each precipitation a portion always remained dissolved by the water, which acted upon the different reagents in a manner similar to the solutions of vegetable extractive matter. The flavour was also bitter, and in some degree aromatic, so that the residua, whether obtained from pit-coal, from Cannel coal, or from asphaltum, seemed to possess properties intermediate between those of resin and those of the vegetable extractive substance. They appeared, however, to be removed only by a very few degrees from the tanning substance ; for if digested in a small quantity of nitric acid, and subsequently evaporated, they were immediately converted into it ; or if digested with sulphuric acid, they speedily became reduced to coal.

#### § IV.

In the 5th section of my second paper, some remarks were made on the decoctions obtained from vegetable substances which had been previously roasted ; and although (excepting one instance) these decoctions did not afford any permanent precipitate with gelatine, yet I have there stated, that I did not think it right to conclude, that similar decoctions made under certain circumstances, might not occasionally possess those properties which characterize the tanning substances. Moreover I also observed in the same paper, that all of those decoctions, upon the addition of a



small portion of nitric acid and subsequent evaporation, became converted into that variety of tanning matter which is produced by the action of nitric acid upon carbonaceous substances. I have since extended these experiments, and shall here give some account of them.

1. 200 grains of the fresh peels of horse chestnuts were digested for about 12 hours in three ounces of distilled water. The liquor was of a pale brown, and formed a slight pale brown precipitate when solution of isinglass was added to it.

2. 200 grains of the same peels were moderately roasted, and being afterwards digested with three ounces of water, formed a dark brown decoction, which was not rendered turbid by gelatine.

3. The above-mentioned roasted peels, after the termination of the preceding experiment, were added to the remainder of the filtrated liquor. A quarter of an ounce of nitric acid was poured upon the whole, which was then digested and evaporated to dryness. The mass was afterwards infused in water, and a dark reddish-brown liquid was obtained, which copiously precipitated solution of isinglass.

4. 200 grains of horse chestnuts, from which the peels employed in the former experiments had been taken, were bruised, and were digested with three ounces of water. The liquor was turbid, and of a pale red colour. It was filtrated, and some solution of isinglass was added, but without any effect.

5. 200 grains of the same horse chestnuts were moderately roasted, and being treated as above described with water, yielded a dark brown decoction which was not rendered turbid by isinglass.

6. The horse chestnuts, which had been employed in the preceding experiment with the remaining liquor, were digested with a quarter of an ounce of nitric acid until the whole was become dry. Water was then poured upon it, was digested, and a dark brown liquid was formed, which afforded a considerable precipitate by the addition of solution of isinglass.

From these experiments it appears, that the small portion

of tannin which the horse chestnut peels originally contained, was destroyed by the process of roasting; that the brown decoction subsequently obtained from the roasted peels and from the horse chestnuts, did not act upon gelatine; but that these were speedily converted into the artificial tanning substance, by the addition of a small portion of nitric acid and subsequent evaporation.

The first preparations of the artificial tanning substance which have been mentioned in the former papers, were made from coal of different descriptions digested with nitric acid; and as similar products have been obtained by the same acid from various decoctions of roasted vegetable substances, there cannot be any doubt, that vegetable bodies when roasted, yield solutions by digestion in water, which essentially consist of carbon approaching to the state of coal, although not absolutely converted into it; for, if so, all solubility in water would cease.

But coal is apparently nothing more than carbon oxidized to a certain degree, and may be formed by the humid as well as by the dry way.

Examples have been already stated respecting operations in which sulphuric acid has produced this effect, but the same likewise appears to be produced with some modifications, whenever vegetable matter undergoes the putrefactive process; for when this takes place, as in dunghills, &c. a large proportion of the carbon of the original vegetable substances appears to be combined with oxygen sufficient to communicate to it many of the properties of coal, whilst the compound nevertheless is capable of being dissolved by water with the most perfect facility.

It must not however be understood that by this process all the other elementary principles are separated, so that only the carbon remains combined with oxygen, but merely, that the other principles are so far diminished, that these, namely carbon and oxygen, predominate in a state approaching to coal, although soluble in water.

Such solutions, I have every reason to believe, are nearly similar to those afforded by vegetable substances which have been previously roasted; and although I have examined but  
a few

a few of them, yet I shall relate some experiments which I have lately made on the peels of walnuts.

It is well known that when these are kept in small heaps for a short time, they become soft, and break down into a black mass, which affords a brownish-black liquor. On these I therefore made the following experiments :

1. About one ounce of walnut peels, which were become soft and black, was digested in water.

A dark brown liquor was thus formed, and, being filtrated, was examined by a solution of isinglass, but not any apparent effect was produced.

2. On an equal quantity of the walnut peels, in the same soft black state, a small portion of nitric acid was poured, and after being digested for about five hours, the whole was evaporated to dryness. The residuum was of a brownish orange colour, and yielded a similar coloured solution to water when digested with it. This was filtrated, and upon the addition of solution of isinglass became turbid, and deposited a tough precipitate, which was not dissolved by boiling water.

3. Another portion of the walnut peels was moderately roasted, and was then digested in water; the brown solution was filtrated, and formed a slight precipitate with gelatine.

4. On the residuum of the last experiment, a small quantity of nitric acid was poured, some water was then added, the whole was digested during about five hours, and until it became perfectly dry.

Water formed with this a brown liquor, which yielded a very abundant precipitate by the addition of dissolved isinglass.

Upon these experiments we may remark, that the solution in the first instance contained carbon in a state approaching to coal, for when treated with nitric acid in the second experiment, a portion (although small) was produced of the same tanning substance which is formed from the different kinds of coal by nitric acid.

The third experiment appears to show, that a small quantity

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tity of a substance approaching to tannin was produced by the simple process of roasting; and the fourth experiment corroborates those already described, in which the artificial tanning matter was copiously produced, whenever roasted vegetable substances were treated with nitric acid.

In respect to vegetable substances, especially those which contain tannin, I shall here relate a few other experiments.

It has been remarked in my second paper, that the tannin of galls was immediately destroyed by nitric acid. Since that time, I have made the following additional experiments :

1. 100 grains of galls reduced to powder were infused with four ounces of water, and part of the infusion upon the addition of solution of isinglass afforded (as usual) a copious precipitate of a brownish-white colour.

A quarter of an ounce of nitric acid was added to one ounce of the above infusion, which then was not in any manner affected by the dissolved isinglass.

2. 100 grains of the same galls were slightly roasted, and being digested with four ounces of water, formed a brown liquor, which was filtrated.

Solution of isinglass was then added to a part of the above liquor, and produced a precipitate not very unlike the former, but much less in quantity.

After this, a quarter of an ounce of nitric acid was added to one ounce of the same liquor, and some dissolved isinglass was subsequently poured into it; by which it was rendered turbid, and a small portion of a dark brown precipitate was produced, resembling that which is commonly afforded by the artificial tanning substance.

3. The remainder of the above-mentioned liquor, with the residuum of the roasted galls, were digested with a quarter of an ounce of nitric acid until the whole had become dry. Water was then poured upon it, and formed a dark brown solution, which yielded a copious brown precipitate by the addition of dissolved isinglass.

From these experiments on galls it appears, that the natural tannin contained in them is destroyed by nitric acid; that

that the tannin is also diminished, and (I may add,) is ultimately destroyed by the process of roasting; that when galls have not been so far roasted as to destroy the whole of the tannin, then the remainder of this seems to be destroyed by the addition of nitric acid, whilst at the same time a small portion of the artificial tanning substance is produced; and that this last is always plentifully afforded by roasted galls when digested with nitric acid, similar to other vegetable bodies when thus treated.

These remarks are also partly confirmed by the following experiments upon oak bark.

1. 200 grains of oak bark, reduced into very small fragments, were infused in about four ounces of water, after which the infusion was examined by dissolved isinglass, and yielded a considerable precipitate.

2. 200 grains of the same sort of bark were slightly roasted, and afterwards digested in water; a much darker coloured liquor was obtained than in the former case; but although it afforded precipitates by the addition of muriate of tin, acetite of lead, and sulphate of iron, yet not the smallest effect was produced by solution of isinglass.

3. The residuum, with the remaining part of the above-mentioned liquor, was then digested with a small portion of nitric acid; this was completely evaporated, and a brown solution was formed by water, which abundantly precipitated gelatine.

4. One ounce of oak bark, reduced into very small fragments, was repeatedly digested in different portions of water until the whole of its tannin was extracted. The residuum or exhausted bark (as it is called by the tanners) was dried, and was afterwards moderately roasted. It was then moistened with diluted nitric acid, which was evaporated in a heat not much exceeding 300° until the bark was become perfectly dry. This was digested in water, and speedily formed a yellowish-brown liquor, which abundantly precipitated gelatine.

5. The bark, which after being exhausted of its natural tannin had thus afforded the artificial tanning substance,

stance, was repeatedly treated with water until the whole of this last was extracted. The bark was then again slightly roasted, was again moistened with nitric acid, and was gently heated and dried as before. Water being poured on it and digested, formed a brown solution, which copiously precipitated gelatine.

6. The whole of the artificial tanning substance was extracted by different portions of water, and the remainder of the bark thus exhausted, was again treated in the manner above described, and again afforded a considerable quantity of the tanning substance, so that these processes evidently might have been continued until the whole of the bark had been converted into it.

This might also have been accomplished, if in the first instance the exhausted bark had been converted into charcoal, and digested in nitric acid, as described in my first paper; but then, the effects would have been more slowly produced, and much more nitric acid would have been consumed. I am now therefore fully convinced, not only by the results of the experiments related in this paper, but also by many others which it would have been superfluous to have stated, that the most speedy and most economical of all the processes which I have described, is that of treating roasted vegetable substances in the way which has been mentioned; and considering that all refuse vegetable matter may be thus converted into a tanning substance by means the most simple, and without any expensive apparatus, I cannot help entertaining much hope, that eventually this discovery will be productive of some real public advantage.

[To be continued.]