VI. *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.*

Read January 16, 1806.

§ 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 well edulcorated, 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.

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 fœtida, 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 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 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

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* 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.

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 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 Pensylvania, 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 substances (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 chesnuts 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 chesnuts, 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 chesnuts 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 chesnuts, 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 chesnut peels originally contained, was destroyed by the process of roasting; that the brown decoction subsequently obtained from the roasted peels and from the horse chesnuts, 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 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 shew, that a small quantity 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, (p. 288,) 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 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, 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.

§ V.

In my first Paper I have remarked, that I suspected the tannin of the peat moors to have been produced during the imperfect carbonization of the original vegetable substances. Whether this has been the case, or whether the tannin has at times been afforded by heath and other vegetables growing upon or near the peat, still appears to me to be uncertain; but whatever may be the origin, I never have yet been able to detect any tanning substance in peat, although I have examined a considerable number of varieties, some from Berkshire, and many from Lancashire, which were obligingly sent to me for this purpose by my friend JOHN WALKER, Esq. F. R. S. Mr. JAMESON has also made the same observation,* so that there cannot be any doubt (whatever the origin of the tanning matter may have been) that it has speedily been extracted and drained from the substances which at first contained it.

This effect is a natural consequence of the great facility with which tannin is dissolved by water, and extends even to the most solid vegetable bodies; I shall here give an example.

In the Philosophical Transactions for 1799, Dr. CORREA DE SERRA has given an account of a submarine forest at Sutton, on the coast of Lincolnshire, where submerged vegetables are found in great abundance, including trees of different descriptions, especially birch, fir, and oak. At the time when I was engaged in those experiments on the Bovey coal, and other substances of a similar nature, which have been printed in the Philosophical Transactions for 1804, Sir JOSEPH BANKS

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* An Outline of the Mineralogy of the Shetland Islands, &c. 8vo. edition, p. 174.

had the goodness to send me a piece of the oak, which was perfect in all of its vegetable characters, and did not appear to have suffered any change excepting, that it was harder, and of a darker colour than recent oak wood. From some experiments which I then made, I found, that after incineration it afforded potash, similar to the recent wood, and contrary to substances like the Bovey coal, which retain the vegetable external characters, although imperfectly converted into coal.*

In the course of my experiments on tannin, I reduced about an ounce of this submerged oak into shavings, and digested them in water. A brown decoction was formed, which with muriate of tin afforded a pale brown precipitate; with acetite of lead, a precipitate of a deeper brown; with sulphate of iron, a copious brownish-black precipitate; but with solution of isinglass not any effect was produced.

The tannin of this oak wood, had therefore either been separated by solution, or had been decomposed; so that the only substance which remained capable of being dissolved by water, was the extractive matter. This last, in the present case, was most probably the original extractive matter of the oak, but in some other instances, (such, for example, as that which was found in the alder leaves contained in the Iceland schistus,†) I am much inclined to believe, that an extractive substance of secondary formation, if I may be permitted to employ such a term, is produced during the process of carbonization. If a substance, therefore, so compact and solid as oak timber can by long submersion be deprived of its tannin, it naturally follows that the same effect must be more speedily produced by the action of water on the smaller vegetable

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* Phil. Trans. for 1804, p. 399.

† Ibid. p. 391.

bodies, which present an extensive surface, and also on porous and bibulous substances such as peat.

But although peat, as I have already observed, does not contain any tannin, yet the imperfect carbonization which it has undergone, renders it like the roasted ligneous bodies, peculiarly susceptible of being converted into the artificial tanning substance when exposed to the action of nitric acid. It would be useless to enter into a detail of the different experiments which I have made upon it, as they were similar to those already related, and I shall therefore only here state, that when seven ounces of well dried peat had been twice moistened, and digested with diluted nitric acid, (to the amount of rather more than two ounces,) and subsequently dried, I obtained by water a solution of the artificial tanning substance, which when evaporated to dryness weighed two ounces. I am convinced, that much more might have been obtained from the residuum of the peat, had I thought proper to have repeated the operation; and I am also certain, that less nitric acid would have been sufficient, had the process been conducted in close vessels, and with other economical precautions, which at that time, were for the sake of expedition and convenience omitted.

§ VI.

It has been generally stated, even by modern chemists, that the acids act but little, if at all, upon resinous substances.

The contrary has however been proved, not only in the three Papers upon the present subject, but also in some others which I have formerly had the honour to lay before this learned Society.

In my experiments on lac, printed in the Phil. Trans. for 1804, p. 208, I have particularly endeavoured to shew, how powerfully the acetic acid acts upon resin, gluten, and some other substances; so that it may justly be regarded, as a valuable agent in the chemical analysis of vegetable bodies. In this point of view, it is as a solvent to be the more highly appreciated, because it appears to dissolve the resins, &c. without affecting their respective qualities, and thus by proper precipitants, these substances may be separated from it pure and unaltered.

I am induced therefore to consider acetic acid to be the true acid solvent of the resinous substances, as it dissolves them speedily, without producing any apparent subsequent change in their natural properties.

Sulphuric acid also, almost immediately dissolves the resins, balsams, &c. and forms transparent brown or sometimes crimson solutions, the latter colour being most commonly characteristic of the balsams.

These solutions, however, are different from those made in the acetic acid, by not being permanent, for from the moment when the solution is completed, progressive alterations appear to be produced in the body which is dissolved; thus turpentine is almost immediately converted into resin, then into the third variety of the tanning substance, and lastly into coal.

Without being under the necessity of adducing other examples, we may therefore state sulphuric acid to be a solvent of the resinous substances, but which continues afterwards to act on their principles, so as to decompose them, coal being the ultimate product.

Nitric acid, as I have shewn in the course of these Papers, and likewise on some former occasions, dissolves the resins, but the progress of its effects seems to be conversely that of sulphuric acid; in the latter case, solution precedes decomposition; but when nitric acid is employed, decomposition to a certain degree precedes solution; for it at first converts the resins into a pale orange-coloured brittle porous substance, then into a product, which apparently possesses the intermediate characters of vegetable extractive matter and of resin, and lastly, this is converted into the first variety of the tanning substance, beyond which I have not been able to effect any change.

As coal therefore appears to be the ultimate effect produced by sulphuric acid upon the resinous bodies, so does the first variety of the tanning substance seem to be the terminating product afforded by the same when acted upon by nitric acid. This effect of nitric acid has been already amply discussed, neither does it appear necessary that I should here repeat the remarks which have been made on some of the simultaneous products, such as the vegetable acids; but amongst the effects produced by sulphuric acid, the coal which is formed seems to merit some attention.

§ VII.

After the tanning substance and the other products had been obtained from the resins, balsams, &c. which have been mentioned in the beginning of this Paper, the following proportions of coal remained.*

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* The weight of the coal obtained from each of the above mentioned substances, was estimated after the complete separation of every other product, and after the moisture had been expelled by a red heat, in close vessels.

	Coal.
100 grains of Copal	67 grains.
——— Mastich	66
——— Balsam of Peru	64
——— Elemi	63
——— Tacamahac	62
——— Guaiacum	58
——— Gum ammoniac	58
——— Amber	56
——— Olive oil	55
——— Balsam of Tolu	54
——— Asa fœtida	51
——— Wax	50
——— Dragon's blood	48
——— Benzoin	48
——— Olibanum	44
——— Myrrh	40
——— Asphaltum	40
——— Gamboge	31
——— Elastic bitumen	31
——— Gum arabic	29
——— Liquorice	25
——— Manna	25
——— Tragacanth	22
——— Caoutchouc	12 *

The coal obtained from the resinous bodies by means of sulphuric acid, is in a much greater proportion, than when

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* Caoutchouc and elastic bitumen were only superficially carbonized by the sulphuric acid, so that the proportion of coal as above stated, is considerably less than that, which in reality might have been obtained from them.

equal quantities of those substances are exposed to simple distillation.

For, (as I have stated in my first Paper,) 100 grains of common resin by the humid process afforded 43 of coal, which after a red heat still weighed 30 grains.

But the same quantity of resin by distillation, only yielded $\frac{3}{4}$ of a grain of coal.

100 grains of mastich, by the first method, afforded 66 grains of coal.

100 grains of the same mastich only gave $4\frac{1}{2}$ grains of coal when simply distilled.

And 100 grains of amber, when treated with sulphuric acid, yielded 56 grains of coal.

But from 100 grains of the same amber when distilled, only $3\frac{1}{2}$ grains could be obtained.

Many other examples might be adduced, but these appear to be sufficient; and I must here observe, that the case is very different in respect to the gums, for the difference between the proportions of coal obtained from them by the humid and dry ways is not very considerable, although it is always the greatest in the former process, when conducted with precaution. Moreover it is to be remarked, that in either process, variations in the quantity of coal are produced by difference of temperature, by the figure and size of the vessels, and many other circumstances.

But it is not only in the proportion, that there is so great a difference between the coal obtained from the resinous substances by the humid way or by fire, for the quality is also most commonly different; and this not only applies to the resins but also to ligneous matter.

The coal obtained by the humid process from many of the resins, was shining, hard, and occasionally iridescent. Few of the coals obtained from the same bodies by fire had any of these properties. The combustion of the former was slow in the manner of some of the mineral coals, whilst on the contrary the latter were speedily consumed like charcoal. This difference I was at first inclined to attribute to a small portion of the acid which might not have been completely separated, and I therefore purposely made some experiments which convinced me that this was not the case.

Having remarked this difference in the coals afforded by the resins, I was desirous to make some comparative experiments on wood, and for this purpose I selected oak.

1.

On 480 grains of oak sawdust I poured two ounces of sulphuric acid diluted with six ounces of water, and placed the matrass on a sand-bath, where it remained from the beginning of last June to the end of September. During this time, the sand-bath had very seldom been heated, but the vessel was occasionally shaken.

At the end of the period above mentioned, six ounces of boiling water were added, and the whole being poured upon a filter, was repeatedly washed, and was afterwards dried on a sand-bath in a heat not much exceeding 300°.

The sawdust appeared to be reduced to a granulated coal, partly pulverulent, and partly clotted; the whole weighed 210 grains.

105 grains of this coal were put into a platina crucible, and were exposed to a red heat under a muffle. At the same

time, an equal quantity of charcoal made from the same oak sawdust, was placed in another vessel by the side of the former.

The charcoal was speedily consumed, and left some brownish-white ashes, which as usual, afforded alkali, with a trace of a sulphate, which was probably sulphate of potash.

On the contrary, the coal formed by the humid way, burned without flame, similar to the Kilkenny coal, and others which do not contain bitumen. It was very slowly consumed, like the mineral coals above mentioned, and left some pale red ashes, which weighed 2 grains. These ashes *did not yield* the smallest vestige of *alkali*, and the only saline substance which could be obtained, was a very small portion of sulphate of potash, which did not amount to more than $\frac{1}{5}$ of a grain; and it is probable, that had the coal been more copiously washed, even this small portion of the neutral salt would not have been obtained.

2.

At the time when the preceding experiment was began, I also put 480 grains of the oak sawdust into another matrass, and having added four ounces of common muriatic acid, the whole was suffered to remain during the period which has been mentioned.

At the end of the four months, the remainder of the acid was for the greater part driven off by heat not exceeding 300°. The sawdust then had the appearance of a brownish-black mass, on which about a pint of boiling distilled water was poured; the whole was decanted into a filter, was repeatedly washed, and was afterwards dried without heat. The sawdust then appeared, as I have observed, brownish-black, and was pulverulent. It burned with some flame, emitted still a slight vegetable odour, and was reduced to ashes much sooner than the coal formed by sulphuric acid, but not so speedily as the oak charcoal. The ashes had an ochraceous appearance, and were almost devoid of any saline substance, excepting a very slight trace of muriate of potash.

These two experiments therefore prove,

1st. That wood may by sulphuric acid be converted into a coal which in its properties is very different from charcoal, although prepared from the same sort of wood; and that the coal thus formed by the action of sulphuric acid, resembles by its mode of burning, and by not affording any alkali when reduced to ashes, those mineral coals which are devoid of bitumen.

2dly. That wood may also be converted into a sort of coal by muriatic acid, but in this case some of the vegetable characters remain, although, like the former, not any alkali can be obtained from the ashes.

§ VIII.

Four different solutions have been proposed respecting that difficult problem in the natural history of minerals, *the origin and formation of coal.*

The first is, that pit-coal is an earth or stone chiefly of the argillaceous genus, penetrated and impregnated with bitumen.

But Mr. KIRWAN very justly remarks, that the insufficiency of this solution is demonstrated by Kilkenny and other coals which are devoid of bitumen, and also that the quantity of earthy or stony matter in the most bituminous coals bears no proportion to the weight of them.*

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* Geological Essays, p. 316.

The second and most prevailing opinion is, that mineral coal is of vegetable origin, that the vegetable bodies have, subsequent to their being buried under vast strata of earth, been mineralized by some unknown process, of which, sulphuric acid has probably been the principal agent, and that by means of this acid, the oils of the different species of wood have been converted into bitumen, and a coaly substance has been formed.

The third opinion is that of ARDUINO; who conceives coal to be entirely of marine formation, and to have originated from the fat and unctuous matter of the numerous tribes of animals that inhabit the ocean.

And the fourth is Mr. KIRWAN'S opinion, who considers coal and bitumen to have been derived from the primordial chaotic fluid.*

The limits of this Paper will not permit me to enter into the various arguments and facts which have been adduced in the support of these different opinions; but the second, or that which regards the vegetable substances as the principal origin of coal, seems by much the most probable, because it is corroborated by the greater number of geological facts, as well as by many experimental results. Most of the former have however been stated in different works, and I shall therefore only notice a few of the latter which have occurred in the course of my experiments.

The observations of Dr. CORREA DE SERRA on the wood of the submarine forest at Sutton, on the coast of Lincolnshire, together with many similar accounts which have been published in the Philosophical Transactions and other works, demonstrate in the most satisfactory manner, that whether

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* Geological Essays, p. 327.

vegetables are totally or partially buried under the waves or under the earth, they are not merely by such means converted even into the most imperfect sort of coal.* Some process therefore independent of these circumstances must have taken place, in order that the vegetable substances, such as ligneous matter, resin, oil, &c. should become coal and bitumen.

In a former Paper I have endeavoured to shew, that these changes are progressive, and having noticed the perfect state of the submerged wood at Sutton and other places, I next described the qualities of the different kinds of Bovey coal, which exhibit a series of gradual changes from bodies which retain the vegetable structure and texture, although imperfectly carbonized, to others in which almost the complete characters of the common mineral or pit-coal are absolutely established.

From the alder leaves in the schistus from Iceland, I obtained extractive vegetable matter, and although this was not

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* In my Paper, " *On the Change of some of the proximate Principles of Vegetables " into Bitumen,*" I have quoted the remarks of BERGMAN, VON TROIL, and others, on the compressed state of the trunks of the trees which have been converted into surturbrand, Bovey coal, and similar substances. The same observation has been also made by Dr. CORREA DE SERRA respecting the timber of the submarine forest at Sutton; and this is the more remarkable, as the submerged vegetables at Sutton do not exhibit any appearance of carbonization.

Dr. CORREA says, " In general the trunks, branches, and roots of the decayed " trees, were *considerably flattened*; which is a phenomenon observed in the surtur- " brand or fossil wood of Iceland, and which SCHEUCHZER remarked also in the " fossil wood found in the neighbourhood of the lake of Thun, in Switzerland." Phil. Trans. 1799, p. 147.

afforded by the varieties of Bovey coal, yet these, as well as the alder leaves, and also a coal like that of Bovey, found in Sussex, at Newick Park, (an estate belonging to Sir ELIJAH IMPEY,) and also the surturbrand of Iceland, yielded some resin, which at Bovey is likewise found in distinct masses, intermixed with the strata of coal, and combined with asphaltum, in the proportion of about 41 parts of the latter with 55 of resin.*

Now, exclusive of the other vegetable characters which are so evident in many of the varieties of Bovey coal, of the Sussex coal, of surturbrand, &c. &c. the presence of resin must be regarded as a strong fact; for this substance has always been attributed to the organized bodies, particularly to those of the vegetable kingdom, and I do not know of any instance, previous to my own experiments, in which, resin had been discovered as constituting part of any of the different species and varieties of coal.

From the external vegetable characters possessed by the Bovey coal, the Sussex coal, the surturbrand, and many others, together with the resin, (allowed to be exclusively a vegetable substance, or at least one which only appertains to the organized natural bodies,) there cannot be any doubt, that such coals have been formed from wood and other substances belonging to the vegetable kingdom.

But some mineralogists attempt to draw a line of separation between the coals above mentioned and the others, which therefore they call the true mineral coals.

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* Observations on the Change of some of the proximate Principles of Vegetables into Bitumen. Phil. Trans. 1804, p. 405.

This opinion may in some degree be refuted even from the specimens afforded by the Bovey coal-pits, where, as I have observed, a regular gradation may be seen from wood which is but very imperfectly carbonized, to the substance called stone coal, which in every respect appears to be most nearly if not absolutely similar to the common pit-coals.*

It may however be objected, that such a transition is peculiar to this and similar places, and that the pit-coal found in other situations, where nothing resembling the Bovey coal can be discovered, is in reality of a different nature.

But this objection I think may be answered by the results of those experiments on pit-coal, Cannel coal, and asphaltum, which I have related in the third section of this Paper; for when these were subjected to the action of nitric acid not too long continued, it was found, that the acid first dissolved the principal part of the carbonaceous matter, and if then the process was stopped, there remained a substance in a proportion corresponding to that of the bitumen either in the pit-coal, or principally forming the Cannel coal and asphaltum, which although not absolutely in the state of resin, was however in a state intermediate between it and the vegetable extractive matter.

Moreover I have stated, that under similar circumstances, a substance possessing in a great measure the same properties, may be obtained from the known vegetable resins by the action of nitric acid.

When therefore, these facts are added to that of the

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* Phil. Trans. 1804, p. 398.

natural mixture of resin and asphaltum which is found with the Bovey coal, we to all appearance have almost positive proof that the pit-coals are of vegetable origin.

True it is indeed, that bitumen has never been formed by any artificial process hitherto devised, from the resins or other vegetable substances. I have myself attempted it in various ways without success, for although I occasionally obtained products which resembled it somewhat in odour when burned, and other properties, yet the effects of alcohol or water always proved these products not to be bitumen.

But synthesis of natural products, although required in strict chemical demonstration, is (as we have but too often occasion to know) seldom to be attained, especially when operations are performed on bodies whose component parts are liable to an infinite series of variations in their proportions, qualities, and mode of combination.

Considering therefore, that bitumen and resin afford by certain operations similar products, that resin and bitumen are found blended together by nature, and that this mixed substance accompanies a species of coal which in many parts still exhibits its vegetable origin, whilst in others it passes into pit-coal, we may with the greatest probability conclude, that bitumen is a modification of the resinous and oily parts of vegetables, produced by some process of nature, which has operated by slow and gradual means on immense masses, so that even if we were acquainted with the process, we should scarcely be able to imitate its effects, from the want of time, and deficiency in the bulk of materials.

But although bitumen cannot at present be artificially formed from the resinous and other vegetable substances by any of the known chemical processes, yet there is every reason to believe, that the agent employed by nature in the formation of coal and bitumen has been either muriatic or sulphuric acid; and when it is considered, that common salt is never found in coal mines except when in the vicinity of salt springs, whilst on the contrary, pyrites, sulphate of iron, and alum, most commonly are present;* these facts, together with the sulphureous odour emitted by most of the mineral coals when burned, appear strongly to evince the agency of the latter. That this has been the case, seems also to be corroborated, by the great resemblance which (as has been previously stated) the coals formed artificially from many vegetable substances bear to the mineral coals, especially as the similarity is not confined to external characters, but extends to other properties.

By the action of sulphuric acid on vegetable bodies, a much greater portion of their carbon is converted into coal than when the same are subjected to the effects of fire.

Several examples respecting the resins, have been mentioned in the seventh section of this Paper, and the result of the experiment made upon oak perfectly accords with them.

Mr. PROUST, in the course of some comparative experiments on the proportions of charcoal afforded by different kinds of wood, obtained 20 *per cent.* from green oak, and 19 *per cent.* from heart of oak.†

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* KIRWAN's Geological Essays, p. 324.

† *Journal de Physique*, 1799, Tome 48, p. 469.

But by sulphuric acid, from 480 grains of oak, I obtained 210 grains, or about 45 *per cent.* of coal, which burned not like the charcoal obtained from the same wood, but like many of the mineral coals; and this was also observed in the combustion of the greater part of the coals obtained by the humid way from resinous substances.

The experiment on oak also appears to refute another objection to the vegetable origin of pit-coal, namely, the total absence of the alkalis, which on the contrary are so constantly obtained from the ligneous parts of vegetables by combustion.* But I have shewn, that when these bodies are carbonized in the humid way either by muriatic or by sulphuric acid, not any alkali can be obtained from the ashes of coals so formed; and this seems also to be a farther proof, that the humid way has been employed in the operations of nature to convert the above mentioned substances into pit-coal; for supposing fire to have been the agent, it does not appear easy to conceive how the alkali could have been destroyed or separated.†

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* KIRWAN'S Geological Essays, p. 320.

† Some have attempted to account for the absence of alkali in the Bovey coal and common pit-coal, by supposing that the vegetable bodies (from which these have been formed) were previously deprived of alkali by simple lixiviation during their immersion in water. But in page 127 of this Paper, I have shewn that the submerged oak of Sutton, although deprived of its tannin, still retained its potash, which certainly would not have been the case if the latter like the former could have been separated from the wood by mere solution. When wood is reduced to ashes, the alkali becomes completely denuded by the destruction of the woody fibre, and consequently may be immediately taken up by water; but when wood is converted into coal in the humid way by means of an acid, then it seems to me that two effects

Every circumstance seems therefore to support the opinion of those who consider the pit-coals as having been formed in the humid way, principally from vegetable bodies, and most probably by the agency of sulphuric acid; and allowing that animal substances may also have contributed to the production of coal, yet this would not militate against the above mentioned opinion, as the effects produced upon them by that acid would in all the essential points be perfectly similar.*

An inquiry into the nature and formation of coal was my first object when I discovered the artificial tanning substance,

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take place; for the intimate combination of the alkali with the woody fibre becomes in a great measure destroyed by the carbonization of the latter, whilst a simultaneous action arises in the affinity between the acid and the alkali; so that if coal has been formed by such means, the alkali must have been separated from the wood in the state of a dissolved neutral salt.

* From the nature of the experiments which have been related in this Paper, I have unavoidably been induced to notice concisely the different opinions on the formation of coal by the humid way; but I did not intend to have mentioned any of those which have been brought forward in favour of the immediate or indirect action of fire, as I only wished to express my sentiments respecting the most probable of the former opinions.

Since however this Paper was written and partly read before the Royal Society, I have been favoured by Sir JAMES HALL, with a copy of his Paper, intitled "*Account of a Series of Experiments shewing the Effects of Compression in modifying the Action of Heat*;" and I am fully of opinion that the scientific world has not for a long time received any communication of more importance, or in which more accuracy, ability, and perseverance have been displayed. The effects which Sir JAMES HALL has produced on carbonate of lime by heat acting under compression, certainly removes a great and at one time apparently insurmountable obstacle to the HUTTONIAN or PLUTONIAN theory, and if they do and considering the importance of the latter, it will not appear surprising, that it should immediately have engaged the principal part of my attention.

In addition to the experiments which have been related in the three Papers upon this subject, I intended to have decomposed the different varieties, to have compared their gases and other products with those of the natural substance called Tannin, and especially to have endeavoured to discover more economical methods of obtaining the artificial product; for, exclusive of speculative science, this appears to be an object of consequence, not only respecting that useful and valuable branch of manufacture to which it immediately relates, but also as the means of preventing, or at least of diminishing, the premature destruction of timber in a country, where, on account of its population, as well as on account of its maritime

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not solve the grand geological problem, they must even, in an insulated point of view, be allowed to have opened a new and unexplored field of research in chemistry as well as in geology.

In the 8th section of this valuable Paper, the author has given an account of some experiments made on leather, horn, and fir sawdust, from which he obtained coal which burned with flame, and which apparently resembled some of the mineral coals. In one case also, he obtained a substance, which in external characters appeared somewhat similar to the mixture of asphaltum and resin found at Bovey, to which I have given the name of Retin-asphaltum. These experiments Sir JAMES HALL intends to resume, and it is my earnest wish that he would do so; for although I am strongly inclined to believe that the mineral coals have generally, if not always, been formed by some humid process, yet it is impossible to foresee the results which may be obtained from animal and vegetable bodies subjected to the effects of heat modified by compression, as the principles of these bodies may be acted upon, and may be made to re-act on each other, under circumstances which until now have not been imagined.

position, every economy in such an article should be most rigidly observed.

But for the present, I intend to relinquish this subject to such as may consider it worthy of attention; whilst, as I have already stated, I entertain very sanguine expectations, that eventually it will prove economically useful; and should any be inclined to pursue the inquiry, I would recommend particular attention to those processes which relate to the roasted vegetable substances, and to peat.

Almost any refuse vegetable matter, such as twigs, dead leaves, &c. will serve for the former; whilst the latter, as I have shewn, does not require to be roasted, and in many, especially the northern counties, peat is found in such abundance, that but a small proportional quantity is consumed in the only useful way to which it has hitherto been applied, namely, fuel.

Before I conclude this Paper I shall also observe, that the experiments which have been described, must be regarded only as a mere sketch of that which may be performed, whilst the facts which have been ascertained respecting the resins, balsams, gum resins, and gums, serve to prove, that much may be expected from regular chemical examinations of these bodies. But such investigations, in order that science may truly be promoted, should be strictly regular: that is, they should not be taken up in a desultory manner, but these substances should be comparatively and systematically examined with all the accuracy which can be employed in the present state of chemical knowledge; for as this knowledge concerning the composition of organized bodies is confessedly very imperfect, I am persuaded, that like other of the sciences, chemistry will be less liable to error, when guided by comparative experiments, and comparative analyses.