XLIII.—*On the Decay of Gutta-percha and Caoutchouc.**

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THE inquiries to which this investigation has given rise have extended over many months, and have included a large number of analyses, but the results obtained may be stated in a small compass, as they are very definite. I have examined numerous samples of gutta-percha cables both injured and sound, which have been in use for several years, and I find in all cases that the deteriorated portions have undergone chemical change, and that change consists in a process of *oxidation*.

Whatever retards or prevents this oxidation, retards or prevents the decay of the gutta-percha, some of the specimens which I examined being as good as new, though they had been manufactured and used electrically for years; whilst others in a few months had become brittle, rotten, and unserviceable. As the general result of these inquiries, I find that whenever the gutta-percha has been completely submerged in water no injurious change has occurred, sea-water appearing to be eminently adapted to the preservation of the gutta-percha. On the other hand, alternate exposure to moisture and dryness, particularly if at the same time the sun's light has access, is rapidly destructive of the gutta-percha, rendering it brittle, friable, and resinous in aspect, and in chemical properties. A gradual absorption of oxygen takes place, and the gutta-percha slowly increases in weight, becoming at the same time proportionately soluble in alcohol, and in dilute solutions of the alkalies. In every instance, however, some portion of the gutta remained unchanged in composition.

My experiments have also been extended to the prolonged action of air, moisture, and light, upon india-rubber, and here also I find that these agents effect analogous changes, though somewhat less rapidly.

* A paper on this subject by Mr. Spiller having recently appeared, it has been thought that the Fellows might be interested in an official report made five years ago to the Joint Committee appointed by the Lords of the Committee of Privy Council for Trade and the Atlantic Telegraph Company, to inquire into the Construction of Submarine Telegraph Cables.—[Ed.]

The caoutchouc, however, instead of becoming brittle, is converted into a glutinous mass, losing its elasticity, increasing in weight to a certain extent, and becoming partially soluble in alcohol and diluted alkaline liquids.

These deductions are made from the examination of a number of samples supplied to me partly by Captain Galton and Mr. L. Clark, including specimens of coated telegraphic wires suspended in air, specimens of submarine cables, specimens of wires sunk in the soil under various conditions, besides experiments instituted by myself upon the action of various agents upon gutta-percha, and they include the results of an extended and well-contrived series of experiments made at the works of the Electric Telegraph Company under the direction of Mr. L. Clark.

I will here subjoin an abstract of the principal experimental details, and for the convenience of reference will arrange them under the following distinct heads:—

- 1st. Experiments upon pure gutta-percha.
- 2nd. Experiments upon commercial gutta-percha.
- 3rd. Experiments upon submerged cables.
- 4th. Experiments upon decayed and damaged cables exposed in air and underground under various circumstances.
- 5th. Experiments upon caoutchouc.
- 6th. Experiments upon other compounds.

1. *Experiments on Pure Gutta.*

Pure gutta differs in some of its properties from the commercial gutta. I found on examining the whitest samples purified by Dr. Cattell, that it formed a porous, milk-white mass, wholly soluble in benzol, in ether, in bisulphide of carbon, and in the ordinary solvents of gutta-percha. It is a perfectly pure hydrocarbon probably containing $C_{20}H_{30}$. I found it to consist of—

	Found.	or	$C_{20}H_{30}$.
Carbon	88·96		88·88
Hydrogen	11·04		11·12
	<hr/> 100·00		<hr/> 100·00

When exposed to a temperature of 212° it softens, but does not liquefy; it loses a trace of moisture, and then gradually absorbs

oxygen, becoming brown, brittle, and resinous in appearance. In one specimen the increase in weight amounted to 4·45 per cent. The oxidized portion is insoluble in benzol, which when digested on the brown mass dissolves out a quantity of unaltered gutta, which had been protected from oxidation by the coating of resin.

This resinous mass when thus purified was found to have been produced from the gutta-percha by simple absorption of oxygen, the gutta having in one experiment absorbed more than a fourth of its weight of oxygen from the atmosphere.

2. *Chemical Experiments on Commercial Gutta-percha.*

The gutta-percha of commerce is not a pure proximate vegetable principle, but it consists chiefly of a hydrocarbon, which may for brevity be termed *pure gutta*, or simply gutta, mixed with a product of its oxidation which is in the form of a soft resin, amounting to about 15 per cent. in the best commercial samples.

The following is the composition of a piece of ordinary good commercial gutta-percha, taken from a piece of new cable supplied to me by Mr. L. Clark :—

Pure gutta	79·70
Soft resin	15·10
Vegetable fibre.....	2·18
Moisture	2·50
Ash	0·52
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	100·00

The moisture reported in this analysis is mechanically diffused through the mass of the gutta-percha, and seems to have some influence upon its pliability and toughness. 100 parts of the commercial sample when dried at 212° till it ceased to lose weight, deducting the ashes, contained—

Carbon	84·66
Hydrogen	11·15
Oxygen	4·19
	<hr/>
	100·00

This gutta-percha softens and liquefies by a heat of 212° . It is soluble, with the exception of a few flocculi of fibrous matter, in benzol, in bisulphide of carbon, and in ether. Alcohol dissolves none of the pure gutta, but extracts a portion of the soft resin. This resin is an oxidised compound, probably in a transitional condition to a higher stage of oxidation. I found it to consist of—

Carbon	76·15
Hydrogen	11·16
Oxygen	12·69
	<hr/>
	100·00

The true gutta was extracted nearly pure from this sample by dissolving it in benzol, filtering and adding alcohol, when a coagulum of pure gutta was obtained, which was found to consist of—

Carbon	87·22
Hydrogen	12·04
Oxygen	0·74
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	100·00

The presence of the small quantity of oxygen in this case was due to a little of the resin which still adhered to the precipitated mass of gutta.

Commercial gutta-percha may be preserved for months, and even years, with little change, either in water or in air, provided light be excluded. This I have found from my own experiments, and the results which I have myself obtained are confirmed by experiments made by Mr. Clark. The following are some of the most important of these experiments:—500 grs. of thin sheet gutta were exposed under various conditions at the end of last October at the Electric Cable Works. The various samples were examined on the 2nd of July of this present year (1860).

1. In netting exposed to sun and rain in open air.
2. In a bottle open to the air and light, but excluded from rain.
3. In a bottle open to the air, but excluded from light.
4. In fresh water, open to air and light.
5. In fresh water, open to air excluded from light.
6. In fresh water, excluded from air and light.

7. In sea water, exposed to air and light.
8. In sea water, excluded from light but exposed to air.
9. In sea water, excluding both light and air.

The specimens 4, 5, 6, 7, 8, and 9 were wholly unaltered, with the exception of a slight increase in weight, due to the absorption of water, which they lost again after exposure to the air for an hour or two. The tenacity and structure of the material did not appear to have undergone the slightest change.

No. 2, which had been folded up and introduced into a bottle, the mouth of which was open and inverted, had increased in weight from 500 grs. to 524·5 grs., or about 5 per cent., owing to absorption of oxygen from the air. The outer layers of the sheet, where exposed to light, were brittle and resinous in appearance, but the inner portion, which had been screened from light by the outer folds, was but little altered in texture or appearance.

On examining chemically a portion of the most brittle part, I found a large portion of it to have lost the composition of gutta, and to have become converted into a matter soluble in alcohol, 55 per cent. of the mass being in fact transformed into the resin already spoken of.

The sample No. 3, which had been kept in the dark, had experienced little or no change. It had only increased 2·5 grains in weight, or 0·5 per cent.; and when treated with alcohol gave up 7·4 per cent. of resinous matter to it.

These results agree with those which I made upon gutta-percha which had been exposed to the light of day for the shorter period of two months. This specimen had become quite brittle, had increased in weight 3·6 per cent., and yielded 21·5 per cent. of resinous matter soluble in alcohol; whilst a piece of the same sheet kept in the dark had undergone no sensible change.

Samples of sheet gutta-percha were also subjected in November last to the action of the following liquids, and exposed to diffused daylight :—

A. Boiled linseed oil.		C. Stockholm tar.
B. Linseed oil not boiled.		D. Coal tar.

When examined on the 4th of August, 1860, or at the end of nine months, these liquids were found not to have exerted any perceptible solvent action upon the gutta, which retained its texture and tenacity in all those portions which had been fairly submerged in the liquid, and protected from the light and atmos-

pheric air; but in those portions which had projected into the atmospheric air contained in the jar, where it was also exposed to the effects of diffused daylight, the texture had become rotten, and the material more or less brittle and resinous.

All the liquids above mentioned are calculated to exclude oxygen from the gutta-percha, and thus they are enabled to exert a preservative influence upon it, without, however, in any degree softening or dissolving its texture. Hence they are likely to be highly valuable agents in coating the insulating material.

3. *Experiments on Submarine Cables.*

I have examined several specimens of cable from different lines which have been submerged for periods of time varying from a few weeks to seven years. In no case where the cable has been completely and continuously submerged have I found any sensible deterioration in the quality of the gutta-percha.

No. 1. Holyhead Irish cable (from Captain Galton), taken up in February, 1859, after seven years' submergence.

No. 2, *a. b. c.* Three specimens from the Dutch line, from Orfordness to Schevening (Mr. L. Clark), submerged five years, raised in August, 1859.

This cable was enclosed in a coating of galvanized iron wire, and contained a single wire of copper in gutta, bound round with hemp and tape soaked in boiled linseed oil, tallow, and Stockholm tar.

a. External coating of galvanized wire, not damaged by corrosion. This sample had been buried on the Dutch coast to a small depth in sand.

b. and *c.* Outer galvanized wire much corroded, but the gutta-percha quite sound. The gutta-percha wire had in each of these samples been exposed to the air, out of the metallic casing, for some months, and consequently was drier than the sample *a*, taken from its metallic coating just before it was analysed.

No. 3. Cable off Portland (Captain Galton); down for seven months; composed of seven thin copper wires twisted into a strand covered with tar, then coated with gutta-percha, without any metallic protecting envelope.

No. 4. Cable from line between Candia and Alexandria (Captain Galton). Construction similar to the last; it showed superficial

erosions of the gutta-percha after submergence for a few weeks; but the composition of the gutta was unchanged.

No. 5. New gutta-percha covered wire (Mr. L. Clark); never used.

The only chemical difference perceptible in these different specimens was in the quantity of water mechanically retained in each.

100 parts of each contained :—

	1.	2.			3.	4.	5.
		a.	b.	c.			
Water	0·84	3·36	1·75	1·49	4·8	0·96	2·50
Ash	1·05	..	..	0·76	3·52	0·75	0·50

4. *Experiments upon damaged Cables suspended in Air or placed underground.*

Of damaged cables I have had various specimens for examination.

1 to 6. Six samples, described by Mr. Saward in his evidence before the Committee, January 12, 1860.

1. Buried in chalky or gravelly soil, coated with a white, friable crust of altered gutta-percha. This was very brittle, and contained 35 per cent. of resin; this resin contained 17 per cent. of oxygen combined with a hydrocarbon of the same composition as pure gutta.

2. Was in soil exposed to leakage of gas-pipes, and also was resinous and brittle, but less so than No. 1.

3. Was described as pulpy when raised, as if fermenting; taken from ground into which drainage from oak trees or posts occurred. When forwarded to me it was hard and tough, the copper wire within was slightly corroded and adhered to the gutta-percha, the channel around the wire lined with a pale brown powder. This powder contained traces of copper. It appears to consist of gutta-percha, as it was almost wholly soluble in benzol, and was insoluble in alcohol. The material in this case seemed to have undergone comparatively little permanent change, although so very different in appearance from ordinary gutta-percha, when it was taken up. It fused below 212°. It had been painted with some pigment

containing lead, and on burning left an ash amounting to 1·87 per cent.

4. Not very brittle, taken from iron pipes.

5. Exposed to a dry heat near a baker's oven; coated with red lead.

6. Exposed to a dry heat (exact source not indicated). This was extremely brittle, could be powdered without difficulty, and was almost converted into a resinous substance. It fused below 212°, it left 1·03 per cent. of ash when burnt, and appeared to have been coated with some pigment.

In all these samples those which were most brittle contained the oxidized resinous body in largest proportion. This resinous substance varied somewhat in the proportion of oxygen which it contained in the different samples, but presented the same general properties. It was soluble in cold alcohol, and still more largely in boiling alcohol; was insoluble in ether, and but sparingly in benzol; diluted alkaline leys dissolved it with facility, and the solution coagulated on the addition of an acid in excess.

7 and 8. Samples of gutta-percha covered wire taken from a tunnel in the Stour valley, placed in the tunnel in 1850 (Mr. L. Clark). One portion of this, A, was comparatively little injured; the other, B, was brittle and rotten. This sample had been coated with some pigment containing lead.

It would be useless to cite in detail the various analyses which I have made of these several samples, or to give the numbers obtained for the proportion of moisture, ash, and resin which they contained, or to quote the proportions of carbon, hydrogen, and oxygen ascertained to exist in the altered portion, as contrasted with the unchanged portion, present in each sample.

It may be stated generally, that wherever the proportion of resin was greatest, the sample of gutta exhibited the greatest degree of brittleness; and this brittleness was always found to be most marked in the specimens which had experienced the greatest degree of oxidation; and further, that these changes appeared to occur most rapidly and decidedly in those points where the gutta-percha was alternately wet and dry.

5. *Experiments on Caoutchouc.*

The caoutchouc of commerce is, like gutta, not a pure vegetable principle, and consists of a hydrocarbon of definite composition,

mixed with a small quantity of resin, the amount of which varies in different specimens.

The following are the results of my analysis of a sample of pure unmanufactured Para rubber, compared with a sample of good sheet masticated or manufactured rubber.

	Virgin.		Masticated.
Pure caoutchouc	96·6		96·64
Moisture.....	1·3		0·82
Resin	1·8		2·06
Ash.....	0·3		0·48
	<hr/>		<hr/>
	100·0		100·00

Or, deducting moisture and ash, its elementary composition gave—

	Virgin.		Masticated.
Carbon	85·82		85·53
Hydrogen.....	11·11		12·06
Oxygen	3·07		2·41
	<hr/>		<hr/>
	100·00		100·00

Caoutchouc, like gutta-percha, is, as already stated, liable to deterioration, by exposure to the action of oxygen in the presence of solar light, but the gum is less rapidly injured if exposed to their influence in the native state, than if it has been previously masticated. When subjected to the action of air excluded from light, it does not experience any marked change, even during very long periods. It is, however, important to observe that the masticated rubber is much more porous than the unmanufactured caoutchouc. When immersed in water, caoutchouc absorbs a much larger quantity of this liquid than gutta-percha, and the masticated much more than the unmanufactured or virgin rubber. I subjoin the results of my examination of some samples submitted to experiment by Mr. L. Clark.

A.—*Virgin Para Rubber, Finest Quality.*

500 grains of this was exposed in each experiment, in the form of a narrow tape-like strip of rubber, which had been stretched while hot and suddenly cooled. It was of a very pale brown colour. The various samples were submitted to experiment at the

end of October, 1859, and were examined nine months afterwards (August 4th, 1860).

No. 1, which had been exposed in netting, in the open air, to sun and rain, had become blackened and rotten, but was neither sticky nor crumbled, had increased in weight 34·5 grains or 7 per cent.

No. 2 was exposed in the air and light, but kept dry in a bottle placed mouth downwards; it had increased in weight 14 grains, or 2·8 per cent., by absorption of oxygen, and had become brown, soft, and sticky, especially in the parts most exposed to light. It gave up 11·81 per cent. of an oxidized, soft, and viscous resin to alcohol. The annexed analysis will give an idea of the composition of the resin thus formed:—

Carbon	67·23
Hydrogen	9·54
Oxygen	23·23
	<hr/>
	100·00

The proportion of oxygen differs a little in different samples.

No. 3, which was exposed to diffused light in fresh water in an open bottle, had become white and opaque from the absorption of moisture, and had increased 86 grains, or 17 per cent., but it had experienced no other alteration in chemical properties, and when dried resumed its original characters.

No. 4, exposed in sea-water in an open bottle to diffused light, had absorbed 3·6 per cent. of its weight of water, but was only a little altered in appearance, not in chemical composition.

B.—*Masticated Rubber, Sheet, Best Quality.*

A similar series of experiments was made simultaneously upon masticated sheet caoutchouc.

No. 1, exposed to sun and rain, had collected into a sticky mass, which had lost its tenacity and elasticity.

No. 2, in the inverted bottle exposed to diffused light and air, had increased in weight 8 grains, or 1·6 per cent., and had collected into a lump, which was viscous, and had lost its elasticity, especially in the parts most exposed to the action of light. When treated with alcohol it was found to yield 12·64 per cent. of its weight of

resinous matter to this solvent. These changes were in marked contrast to No. 3, which was kept in a glass bottle in the dark for the same period, but exposed to the air freely. It had increased in weight only 0·6 per cent., did not show any sign of alteration in tenacity or elasticity, and yielded to alcohol 2·0 per cent. of resin only.

No. 4, a sheet of the same rubber immersed in fresh water, open to the air and diffused light, had increased 87 per cent. by absorption of water, that is to say, it had nearly doubled its weight. It had become white, opaque, slimy, and sticky when pressed, and allowed water to be squeezed out by pressure. It lost weight rapidly by drying when exposed to the air.

No. 5, similar to the last, but exposed in sea-water. It was slightly opaque and slimy, but had increased only 5 per cent. in weight by absorption. A second sample, in sea-water in a closed bottle, emitted a smell of sulphuretted hydrogen, and had gained 5·6 per cent. in weight by absorption. Its elasticity and tenacity were not impaired. The gradual permeability of masticated caoutchouc to water was further strikingly shown by enclosing a quantity of acetate of potash in bags made of sheet rubber and accurately sealed. They were then immersed in water, and at the end of nine months the salt in each of the bags was found to have become liquefied by the water which it had absorbed, and the bags had in each case gained in weight several grains.

C.—*A similar Series of Experiments was made with Sheet Rubber, vulcanized.*

1. The sheet exposed in the netting to the sun and rain had lost 2 per cent. in weight; it was scarcely less tenacious than at first.

2. A similar sheet in fresh water absorbed 19 per cent., but was not otherwise altered.

3. A similar sheet in sea-water was rather more slimy, and had only gained 1·6 per cent. in weight.

Each of the three substances, viz., natural, masticated, and vulcanized rubber were submitted to the action of the following solvents for nine months:—

- A. Boiled linseed oil.
- B. Unboiled linseed oil.
- C. Stockholm tar.

The *virgin rubber* had resisted the action of the solvents almost perfectly, retaining its toughness, excepting in those parts which were above the surface of the liquid and exposed to light. In the tar this rubber had contracted spontaneously, but was still strong and elastic.

The *masticated rubber* was in each instance greatly swollen and gelatinized, and indeed in the case of the unboiled oil was completely dissolved.

The *vulcanized rubber* had also lost its tenacity, and had become swollen and gelatinous, but retained its form and a certain degree of elasticity.

A sample of india-rubber cable (from Captain Galton), which contained six strands of copper wire, each coated with rubber, then bound round with tape and again with rubber, had experienced a singular change, having become, *where in contact with the wire*, quite glutinous and sticky. This change, however, did not progress in the specimen which I kept for some months in my room, but the viscosity on the contrary gradually diminished.*

6. *Experiments on other Substances.*

An insulating mixture composed of gutta-percha, shellac, and powdered glass or clay, known as "Wray's Compound" (from Captain Galton), was also submitted to experiment.

Heated to 212° , it softened, but retained its shape. It lost by drying 0.5 per cent. of moisture, and when burnt left 22 per cent. of a white ash, chiefly silicate of alumina. This compound absorbs water but sparingly. 500 grains left in fresh water for six months increased 7.5 grains in weight, or 1.5 per cent., and a similar increase in weight occurred in another experiment where *sea-water* was used.

Sample of Gutta-Percha Cable (from Captain Galton) vulcanized by Mackintosh's Patent.

The wire was found to be blackened on its surface from the action of the sulphur, owing to the formation of sulphide of copper, and traces of copper were found in the gutta-percha covering.

* The quantity of viscous matter was too small to admit of satisfactory analysis, I ascertained, however, that no copper was present in the viscous mass, and that the wire was not corroded. I could not determine whether grease was present in small quantity, as was not unlikely.