

### Conclusions.

The ingestion of water at meal time by two men was accompanied by an increase in the excretion of ammonia which was *directly proportional to the extra volume of water ingested*. Inasmuch as certain experiments have demonstrated that water *stimulates the flow of an acid gastric juice* and as certain other experiments have demonstrated that the formation of acid in the body or the introduction of acid from without produces *an increase in the urinary ammonia excretion*, we feel justified in assuming that the increase in the ammonia excretion observed in our experiments was *due directly to the stimulation of gastric secretion by the ingested water*.

The uniform relationship between the water ingestion and the ammonia output might perhaps be considered as indicating that there was an attempt on the part of the gastric cells to maintain a *uniform acid concentration*.

If we calculate the increased ammonia excretion, on the basis of a 100 cc. increase in the water ingestion, we find that the excretion was a trifle higher during moderate water drinking than during copious water drinking. This would indicate that after a certain limit had been reached in water ingestion each succeeding 100 cc. of water was less efficient as a stimulating factor than were the 100 cc. portions ingested before the limit above mentioned had been reached.

That different organisms may respond differently to identical stimuli was indicated by the fact that the increase in the ammonia output of one subject was 100% greater than that of the other subject, notwithstanding the fact that the increase in the water ingestion was the same in each instance.

That the increase in the ammonia excretion *did not arise from intestinal putrefaction* was indicated by the finding of *lowered indican values* during the period of high water ingestion.

PHILADELPHIA, PA.

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[CONTRIBUTION FROM STEVENS INSTITUTE OF TECHNOLOGY.]

## A REVIEW OF THE PIONEER WORK ON THE SYNTHESIS OF RUBBER.<sup>1</sup>

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Received November 7, 1913.

At a meeting of the chemical society of Heidelberg on May 19, 1906, Prof. E. Knoevenagel<sup>2</sup> presented a paper in which he described two new hydrocarbons, C<sub>8</sub>H<sub>10</sub>, belonging to the Δ<sup>1,3</sup>-butadiene series. One of these hydrocarbons was found to yield a dimolecular polymeride, C<sub>12</sub>H<sub>20</sub>,

<sup>1</sup> Read before the New York Section of The American Chemical Society, Oct. 10, 1913.

<sup>2</sup> *Z. angew. Chem.*, [2] 19, 1330.

and it was suggested that its formation was possibly similar to the formation of dipentene,  $C_{10}H_{16}$ , by the polymerization of isoprene,  $C_5H_8$ .

It was also stated that the investigation of these two hydrocarbons would be continued, especially to determine whether, by other methods of polymerization, it would be possible to prove a relationship between these compounds and the rubber group.

In the discussion following the reading of this paper, Prof. A. Klages<sup>1</sup> stated that he had been occupied for a long time with the study of the homologues and analogues of isoprene, and other hydrocarbons of the butadiene series. He had found that the members of this group almost without exception possess the property of yielding dimolecular compounds when treated with sulfuric acid.

Professor Klages further stated that he had tested a large number of these hydrocarbons, especially with a view to the possibility of converting them into rubber-like substances. Notwithstanding the fact that he had made many experiments with these hydrocarbons, including isoprene, he had never been able to isolate a product having the well-known elasticity and nerve of true rubber, not even from isoprene. Further, the hydrocarbons formed from sorbinic acid, according to Doebner, possess a structure showing the greatest analogy with 1,5-dimethylcyclooctadiene, a substance which Harries describes as the parent hydrocarbon of the rubber series; even these hydrocarbons have never been converted into rubber-like products.

Accordingly, Prof. Klages said it was his opinion that the close relationship of isoprene to rubber, which had up to that time been ascribed to this hydrocarbon, had no justification; and the statements that isoprene can be converted into rubber-like substances do not correspond with the facts, and it was therefore time to strike such statements out of the literature.

On March 12, 1910, in Vienna, Prof. C. Harries<sup>2</sup> delivered a lecture on the chemistry of rubber. During this lecture he stated that until most recent times all experiments on the synthesis of rubber have failed, and Klages has declared that, according to his experiences, it is absolutely impossible to convert isoprene into rubber. Continuing, Prof. Harries stated the following:

"During the past seven years or so, at different times and with many different co-workers, I have repeated the work outlined by Tilden, and have never been able to confirm his results. Also I am advised that the same thing has been done by others with the same negative results. I exhibit here a preparation consisting of isoprene which was saturated with hydrochloric acid gas three months ago; aside from some darkening in color, it is absolutely unaltered. If isoprene is treated with organic acids and is then allowed to stand, there is no appreciable change to be observed even after many months; formic acid alone causes the isoprene to resinify quickly. Therefore, Tilden must have quite accidentally hit upon certain conditions in his experiments, which caused the polymerization of isoprene. But the most important point relative to Tilden's work is that he never proved that he actually had rubber in his hands, for, as I will illustrate later, isoprene may be converted into all sorts of

<sup>1</sup> *Z. angew. Chem.*, [2] **19**, 1330; *Gummi-Ztg.*, **23** (Sept. 21, 1906), 1277.

<sup>2</sup> *Gummi-Ztg.*, **24** (March 18, 1910), 851; see also *Chem. Ztg.*, **34**, 315.

products which might be described as rubber-like, although they really have very little to do with rubber. Thus, after long standing in the presence of air, isoprene certainly becomes viscous, but this is not caused by polymerization; it forms a peroxide which is very explosive when heated. Therefore, in view of my own experiences, I was for a long time of the same opinion as Klages.

"My interest in this particular direction was renewed last summer when, upon the recommendation of Geh. Rat. Hempel of Dresden, I was asked by a large English firm if I was in the position to determine for them whether a certain sample of a rubber-like product was real rubber. This sample was alleged to have been prepared by a process patented in England by a Dr. Heinemann, and the process was said to consist in passing acetylene, ethylene and methyl chloride simultaneously through a red-hot tube. This was alleged to first form isoprene, which was then at once polymerized to rubber. I at once determined that the sample in question really was a true rubber, but its outward appearance was devilishly (*verteufelt*) similar to that of old para-rubber. I advised the firm that the sample in question was actually rubber, but I especially emphasized the fact that before they should take any further steps in the matter, they should be absolutely convinced that the sample sent to me had actually been prepared by Dr. Heinemann's process. For a long time I have taken special pains to repeat this process, and I know that others also have tried to reproduce it; but neither I nor the other chemists have been able to confirm in the slightest particular the statements given in the English patent. If isoprene and rubber can actually be obtained by this process, then there are such special conditions necessary that they should have been clearly stated in the patent, and to anyone who re-discovered these special conditions, I, as a competent judge, would give the right to patent them as new in Germany. As a matter of fact, however, I do not believe that the process works at all; according to our practical experiences it is extremely improbable.

"However, by means of these experiments I came back to isoprene and directed my work to new syntheses of isoprene and to its polymerization. On the first of November, 1909, Geh. Rat. Duisberg of the Elberfeld Farbenfabriken sent me some samples of artificial rubber, which were alleged to have been prepared from isoprene by a process invented by Dr. Fritz Hofmann; the details of the process, however, were not given to me. I was asked to determine whether these samples contained true rubber. I was able to determine that these samples were true rubbers in every particular, and, therefore, artificial rubber was prepared from this side for the first time."

On June 17, 1912, Prof. W. H. Perkin, Jr., read a paper<sup>1</sup> on "The Production and Polymerization of Butadiene, Isoprene, and their Homologues," before the London Section of the Society of Chemical Industry. I quote the following paragraphs from Prof. Perkin's paper:

"As regards the history of this synthesis, it seems to me desirable, in view of statements which have been made abroad, to review the work of earlier investigators, and particularly that of W. A. Tilden in England, and G. Bouchardat in France, in order that I may emphasize the fact,

<sup>1</sup> *J. Soc. Chem. Ind.*, 31, 616.

as I particularly wish to do, that much of the credit of the pioneer work in this subject belongs to this country and to France.

"It is surprising that Prof. C. Harries should doubt whether Tilden really had synthetic rubber in his hands in 1882 and 1884, and should advance the view that certain samples produced in 1909 by Bayer & Co., of Elberfeld, were the first true samples of synthetic rubber. This criticism is quite beside the mark, and the specimens of crude synthetic rubber which Tilden undoubtedly prepared were made many years before Bayer & Co. produced rubber by their process."

"It is of very great interest to notice that an Englishman, Greville Williams, who, in 1860, was the first to isolate isoprene from the products of the destructive distillation of rubber in a fairly pure state, was also the first to observe the transformation of this hydrocarbon into a rubber-like body." "It is true that this substance, which Greville Williams regarded as an oxide, was not at his disposal in sufficient quantity, or purity for him to definitely identify it with rubber (which it undoubtedly contained), but it is clear from his remarks that he considered that both caoutchouc and gutta-percha are polymers of isoprene."

"In 1875 G. Bouchardat showed that isoprene is converted by heating in a sealed tube into a mixture of polymers, including the indefinite substance named colophene, which there can be no doubt contained a considerable proportion of rubber."

"It is a remarkable tribute to Tilden's intuition that he should not only at this early date (1882) have foreseen the successful production of synthetic rubber, but he should also at the same time have suggested the correct formula for isoprene."

"In 1892 Tilden showed for the first time that synthetic rubber is capable of vulcanization and therefore sufficiently resembles natural rubber to be used commercially, if some means could be discovered for producing it in quantity."

"Harries and Klages were tempted, as has already been stated, to throw doubt on the validity of Bouchardat's and Tilden's polymerisation results; this, in spite of the confirmatory work of many other investigators on isoprene and its homologues to which I have already alluded. But no one who is really conversant with the literature of the subject, or who has had the opportunity of inspecting the preparations made by Tilden, can, for a moment, doubt that Tilden had polymerized isoprene to rubber as far back at least as 1884. And similarly there can be no doubt that Bouchardat had synthetic rubber in his hands as far back as 1875."

"I wish to emphasize the fact, which on more than one occasion has been overlooked, that much of the pioneer work in connection with the discovery, production, and with the polymerization of isoprene was carried out in this country."

On September 9, 1912, Geh. Rat. Dr. Carl Duisberg of Elberfeld, Germany delivered his extremely interesting and brilliant address before the Eighth International Congress of Applied Chemistry, in New York City. The subject of this general lecture was "The Latest Achievements and Problems of the Chemical Industry,"<sup>1</sup> and reprints of this lecture were distributed at the time of the address. As I recall it, the

<sup>1</sup> "Transactions and Organization," *Eighth International Congress of Applied Chemistry*, Vol. 28, pages 50 and 86.

address followed almost exactly word for word the text given in the reprint, and I will quote some paragraphs as given in this reprint:

Page 29 of reprint. "I will refer to one of the greatest successes and yet one of the most difficult problems of the chemical industry, *viz.*, the production of synthetic rubber. I am proud of the fact that its production was successfully accomplished in the works which are under my management, and that I was able to follow every stage of this important discovery. Perhaps you would be interested to hear how the whole thing happened, especially as much that is untrue and misleading has appeared in the press during the last few weeks."

Page 30. "By breaking up the very complex molecule which rubber doubtless possesses, by pyrogenetic processes, *i. e.*, by dry distillation, a veritable maze of all kinds of gases, oils and resins was obtained, as well as a colorless fluid resembling benzine, to which the investigators gave the name 'Isoprene.' It was the French scientist Bouchardat who first expressed the belief that this isoprene, which is obtained in very small quantities and in an impure form by the dry distillation of caoutchouc, might be closely and intimately related to caoutchouc itself. This important question was then eagerly discussed for several decades by the scientists of all countries and opinions were sharply divided. As far back as the eighties, the Englishman Tilden claimed to have prepared artificial rubber from isoprene by treatment with hydrochloric acid. But neither Tilden nor his assistants, though they worked strenuously for years, succeeded in repeating the experiments. Moreover, numerous other investigators were unable to confirm the results. Dr. Fritz Hofmann of the Farbenfabriken vorm. Fried. Bayer & Co. is to be regarded as the real discoverer of synthetic rubber, for, by the application of heat, he succeeded, in August, 1909, in polymerizing the isoprene molecules into the complex rubber molecule. Somewhat later Harries discovered independently another method of arriving at the same result. Everyone is now in a position to repeat this exceedingly simple experiment himself, but in order to confirm Hofmann's results, it is necessary to employ *pure* isoprene."

I find that this address was changed in certain points before its final publication in Volume 28, of the Transactions of the Eighth International Congress of Applied Chemistry. The changes occur in the above quoted paragraph commencing with the statement, "Moreover, numerous other investigators," etc. Since these changes are important, I will quote this particular part as printed on pages 113 and 114 of Volume 28:

"Moreover, numerous other investigators, among them our chemists, were unable to confirm the results. In 1894 Tilden found, however, that that isoprene which he had prepared about ten years before, on standing, had partially polymerized into rubber. In this way Tilden in fact was the first discoverer of synthetic rubber. But this method which time has not yet permitted to repeat, is obviously not a commercial one. Dr. Fritz Hofmann of the Farbenfabriken vorm. Fried. Bayer & Co. is to be regarded as the real inventor of synthetic rubber, for, by the application of heat, he succeeded as the first in August, 1909, in polymerizing the isoprene molecules completely into the complex rubber molecule on a technical scale."

Continuing his address, Geh. Rat. Duisberg said: "Isoprene belongs to the butadienes. It was therefore to be assumed at the start that

$\beta$ -methylbutadiene would not hold a peculiar and isolated position among the butadienes in general. It was argued that other members of this interesting group of hydrocarbons would yield analogous and homologous rubbers on being heated." "Exact proof of the existence of the class of isomeric and homologous caoutchouc was also first presented by Elberfeld."

In a paper<sup>1</sup> by Dr. F. M. Perkin, read before the Royal Society of Arts on December 11, 1912, the author referred to the pioneer work on synthetic rubber in the following paragraphs:

"In all probability, Greville Williams (in 1860) had actually produced synthetic rubber."

"The first real proof of the polymerisation of isoprene to form rubber was by Sir William Tilden in 1882."

"It having been shown by Tilden, and confirmed by other workers, that isoprene on polymerisation formed rubber, the chief efforts of investigators in the first place were directed to obtain a satisfactory and cheap method for the preparation of isoprene."

"About 1899 or 1900, Kondakow showed that other members of the isoprene or divinyl series could be polymerised into rubber-like bodies, either by exposure to light, or on keeping, or by means of chemical agents."

In a monograph<sup>2</sup> on 'The Synthesis of Rubber' by Dr. Rudolf Ditmar, published in 1912, the author says:

"The synthesis of rubber was made possible only by the work of Prof. C. Harries explaining the constitution of the rubber molecule. It is true that the synthesis of rubber from isoprene was accomplished long before Harries' work on the constitution of rubber, but without the scientific back-ground furnished by Harries, this synthesis by Bouchardat would be in a sorrowful position." "Owing to Harries' work alone, we can now say 'rubber must be prepared from isoprene;' and since the publication of Harries' work, the syntheses of rubber have proceeded along scientific lines."

"By heating isoprene with dilute acids, Bouchardat, in 1879, obtained an elastic polymeride, which, after boiling with water, possessed the properties of rubber. This first synthesis of rubber by Bouchardat was confirmed by W. A. Tilden and O. Wallach. However, the statements of these investigators agree that it was impossible to determine the experimental conditions necessary for the synthetical preparation of rubber."

"The first useful technical method for the synthesis of rubber was announced, in a patent by the Farbenfabriken vorm. Friedrich Bayer & Co. of Elberfeld under date of September 11, 1909."

In a paper dated November 12, 1912, and published in the *Annalen*<sup>3</sup> on January 30, 1913, Prof. Harries refutes the claim to priority in the field of synthetic rubber advanced by Perkin, Jr. and others. There is much in this paper which I shall wish to quote later on, when considering details, but there is one portion which I think should be given here.

Prof. Harries says: "It is only about two years since my last paper<sup>4</sup>

<sup>1</sup> "Natural and Synthetic Rubber," *J. Roy. Soc. Arts*, 61, 92, 93.

<sup>2</sup> "Die Synthese der Kautschuks," von Dr. Rudolf Ditmar, pp. 3, 24, 25.

<sup>3</sup> *Ann.*, 395, 211.

<sup>4</sup> *Ibid.*, 383, 159.

on synthetic rubber was published, and this paper has produced a remarkable literary activity. For 10 years I believed I was working alone in the field of rubber chemistry, when all at once I discovered that chemists everywhere had been working on the same problems even before my work. However, the publication of these various papers first began to appear after my lecture in Vienna in 1910, in which I mentioned certain eventually successful practical results. But this result of my lecture would have been very welcome, had there not appeared less agreeable features, which probably never before appeared to such an extent in any other field of chemistry; I refer to the introduction of nationalistic motives into scientific research, and to the broadcast discussion of questions of priority in scientific matters in the daily press, or in certain journals which usually are not selected for such discussions.

"What am I to say, when one may see to-day in any newspaper an elaborate account of how Perkin, Jr. has stated in a lecture that English chemists discovered sodium-synthetic rubber six months before I did? I certainly cannot enter into a discussion of priority regarding a scientific question in the daily press!"

"If Russian and English chemists to-day endeavor to especially emphasize the priority of the discoveries in the field of rubber chemistry as strictly Russian or English, then it appears to me a regrettable departure from the customs of the Masters of previous generations, who regarded science as international."

"On July 15, 1912, W. H. Perkin, Jr. delivered a lecture before the London Section of the Society of Chemical Industry, the purport of which in many of its relations challenges contradiction. The purpose of this address is quite apparent, namely, the presentation of the discoveries in the field of rubber and gutta-percha chemistry as purely English accomplishments."

"Really, one can only shake his head as Perkin now seeks to interpret the old, meager statements of Williams relating to the auto-oxidation products of isoprene so that it will appear that Williams really had synthetic rubber in his hands."

In view of these conflicting statements by Klages, Harries, Perkin, Jr., Duisberg, and others, regarding the pioneer work on this subject, it has seemed to me desirable to review, in considerable detail the published work of the earlier investigators. In doing this, I shall quote the exact statements given in the literature, and shall try to quote impartially and in sufficient detail so that each one may arrive at his own conclusion as to the amount of credit due to each of the earlier workers.

Possibly the first important paper on this subject is "On Isoprene and Caoutchine" by the Englishman, C. Greville Williams,<sup>1</sup> published in 1860. In this paper Williams describes certain experiments on the dry distillation of caoutchouc, in which he obtained traces of volatile bases, and two chief distillates, the one boiling between 37° and 44°, the main portion of which distilled between 37° and 38°, and the other boiling between 170° and 180°. The liquid boiling at 37° to 38° was named *isoprene*, while that boiling between 170° and 180° was termed "caoutchine."

<sup>1</sup> *Phil. Trans.*, 1860, 245; *Proceedings of the Royal Society*, 10, 516.

Under the heading, "Action of Atmospheric Oxygen on Isoprene," Williams states the following:

"If isoprene be left in a partly filled bottle for some months, it gradually loses its fluidity, and at last even becomes quite viscid; at the same time it is found to have acquired powerful bleaching properties. It is, in fact, ozonized."

"On submitting ozonized isoprene to distillation, if the temperature be kept as low as is compatible with the volatilisation of the unaltered portion of the oil, a colorless limpid fluid distils over, having the composition and boiling point of pure isoprene. As the operation proceeds the fluid thickens, causing the temperature to rise somewhat suddenly. The ozone at this point instantly begins to act with energy, a cloudy vapour rises, accompanied by an intensely sharp odour, and the contents of the retort instantly solidify to a pure white, spongy, elastic mass, having, when successfully prepared, but slight tendency to adhere to the fingers. When pure, it is opaque; but if allowed to become exposed to the air, especially when warm, it becomes transparent, first on the edges, and subsequently throughout the whole mass. When burnt, it exhales the peculiar odour hitherto considered characteristic of caoutchouc itself. It is not easy to prepare or to preserve this substance of definite composition. If the heat be allowed to rise too rapidly during its formation, it becomes decomposed; and if not heated sufficiently, a portion of the original hydrocarbon obstinately adheres. However prepared, its composition is that of isoprene plus oxygen. If sufficient care be taken, the oxidation is perfectly definite. A specimen prepared with every precaution, and immediately analyzed gave 78.8% of carbon, 10.7% of hydrogen, and 10.5% of oxygen."

"The above-described substance is, it is believed, unique in its characters, whether we regard its composition as the directly formed oxide of a hydrocarbon or the mode of its production by the influence of ozone."

That Williams regarded caoutchouc as in some way related to isoprene and caoutchine (later termed di-isoprene and dipentene), is shown by his statement "On the Composition of Caoutchouc;" he says: "I am anxious to call attention to the fact that the atomic constitution of caoutchouc appears to bear some simple relation to the hydrocarbons resulting from its decomposition by heat. The composition of caoutchouc coincides with that of isoprene and caoutchine, as found by analysis, to a degree which is remarkable when we consider that caoutchouc, in addition to being non-crystalline, is scarcely capable of purification by chemical means."

A review of this paper in the "Proceedings of the Royal Society of London" for the year 1860 states that Williams "considers the action of heat on caoutchouc to be merely the disruption of a polymeric body into substances having a simple relation to the parent hydrocarbon."

Prof. Perkin, Jr., says that this pure white, spongy, elastic mass, described by Williams as an *oxide of isoprene* and not as rubber, "*undoubtedly contained rubber,*" and Perkin, Jr. evidently seeks confirmation of Williams' work in a patent taken out by A. Heinemann of London in 1910. This patent<sup>1</sup> is on a "Method for the Preparation of Rubber from Isoprene," and it contains the following statements:

<sup>1</sup> English Patent, No. 14041, 1910; Deutsche Patentanmeldung, H54443, Kl. 39 b, June 6, 1911.



"This discovery consists in a method for the preparation of rubber by the action of ordinary or nascent oxygen, or ozone, on isoprene. A special characteristic of this discovery consists in the fact that isoprene is first treated with oxygen or ozone, and then heated. On heating, the isoprene first thickens, and then is changed into a substance, which possesses the properties of natural rubber."

Perkin, Jr., says: "this seems to be almost exactly what Greville Williams had described fifty years before."

True; but, in my opinion, this is not sufficient reason for Perkin's assumption that Williams' product "undoubtedly contained rubber." I know of no paper by Perkin, Jr. in which he even attempts to prove that the method described in Williams' paper and in Heinemann's patent actually does give "a substance which possesses the properties of natural rubber." It is hardly safe to base one's conclusions in such a matter on the unverified statement, or patent of another person.

Furthermore, we shall later see where Perkin's use of another Heinemann patent has apparently led Perkin, Jr. into an error, with the result that an injustice was, I think unintentionally, committed against the chemists of Bayer & Co.

In his second paper<sup>1</sup> on the synthetic rubbers, published on January 30, 1913, Prof. Harries refers to Williams' paper and Perkin's comments on it as follows:

"I have previously pointed out that when isoprene is allowed to stand for some time in contact with air in closed bottles, it certainly becomes viscous; however, this treatment does not form rubber, but rather a highly explosive peroxide. If the latter be so heated as to cause an explosion, then it is quite true that an odor similar to that of burning rubber is observed; but the resulting residue does not contain rubber, as Perkin assumes it does. Heinemann's English patent, which Perkin cites to strengthen his claims, does not persuade me to change my views, because it is impossible to regard this man's patent seriously after he states that rubber is produced by heating the reaction-product resulting from the ozonisation of isoprene."

Personally, therefore, I believe it should be especially emphasized that Williams did not say that he prepared rubber, and he certainly gave no proof that his product was rubber, and there has been no subsequent work published to prove that Williams' product was true rubber. To say that his product "*undoubtedly contained rubber*," is at the present time speculation, and we have no right to call him the *discoverer of synthetic rubber*.

The next important work on the synthesis of rubber to be noted is that by the French chemist, G. Bouchardat, published on June 14, 1875, and December 29, 1879. Since this work has caused considerable debate, I think we should first carefully consider Bouchardat's own words. In his first paper,<sup>2</sup> published in 1875, "On the Synthesis of a Terpene," Bouchardat says:

"I subjected isoprene, placed in sealed tubes, to a temperature of 280° to 290° for six hours, and excluded the least traces of air in the tubes by means of an atmosphere of carbon dioxide gas.

<sup>1</sup> *Ann.*, **395**, 217.

<sup>2</sup> *Bull. soc. chim.*, **24**, 108; *Compt. rend.*, **80**, 1446.

"No gas was formed during this action. The product which resulted by the action of heat is entirely changed in its appearance; it is less fluid, viscous; its specific gravity is increased; it no longer boils at a constant temperature of 38°.

"On distillation the product is separated into three chief products, *viz.*, first, a certain proportion of unaltered, original hydrocarbon; second, a hydrocarbon volatile at 170° to 185°; third, products of condensation with a higher boiling point; I have studied chiefly the product volatile at 170° to 185°. The greater part of this distils at 176° to 181°."

"To sum up, isoprene, a hydrocarbon containing only 10 equivalents of carbon, gives, when condensed or polymerized by the action of heat alone, a hydrocarbon containing double the number of carbon atoms, and whose derivatives are identical with those of *terpilene*."

Referring to this paper, Prof. Perkin, Jr. says:

"In 1875, G. Bouchardat showed that isoprene is converted by heating in a sealed tube into a mixture of polymers of isoprene, *viz.*, dipentene, C<sub>10</sub>H<sub>16</sub>, C<sub>15</sub>H<sub>24</sub>, etc., including the indefinite substance named colophene, *which there can be no doubt contained a considerable proportion of rubber.*"  
 "There can be no doubt that Bouchardat had synthetic rubber in his hands as far back as 1875."

In my opinion, there is no justification in Bouchardat's words for such a statement. He most certainly does not mention that his higher boiling product (colophene) contained a *trace of rubber*, not to mention "*a considerable proportion.*"

In the light of Bayer & Co.'s patents of 1909, describing the formation of synthetic rubber by heating synthetic isoprene in sealed vessels at 100° to 200°, it is easy to imagine that Bouchardat might have obtained rubber in 1875 if he had used isoprene of equal purity, and had observed the same conditions of temperatures, etc., which these investigators did some 34 years later. But after reading Bouchardat's paper, there seems to me no reason for believing that he had synthetic rubber in his hands in 1875.

Bouchardat's second paper,<sup>1</sup> published in 1879, is on "The Action of the Halogen Acids on Isoprene, and *The Reproduction of Rubber.*" I quote from this paper the following:

"When dry hydrochloric acid gas is passed slowly through isoprene cooled to 0°, it is partially and slowly absorbed, and yields a mobile liquid, having a brown color. When the product is distilled, it yields some unchanged hydrocarbon, and isoprene mono-hydrochloride, boiling at 86° to 91°.

"Under the conditions, *viz.*, three hours of action, the formation of an appreciable quantity of a substance having a higher boiling point is not observed."

"Hydrochloric acid, in a solution saturated at 0°, acts differently upon isoprene than does the dry gas. One part of isoprene was treated in the cold in a sealed vessel with 12 to 15 parts of the acid. A vigorous reaction, indicated by a notable rise in the temperature of the mixture, took place immediately upon agitation; the whole was left at the room temperature for 15 to 20 days, agitating only from time to time. The contents of the tube were then added to water and submitted to distilla-

<sup>1</sup> *Compt. rend.*, 39, 1117, 1118, 1119.

tion as long as oily drops were obtained. There remained, with the excess of acid water, a solid residue in notable proportions.

"The volatile products resulting from the distillation included no unchanged hydrocarbon; it yielded one-fifth of its volume of a substance boiling at  $85^{\circ}$  to  $91^{\circ}$ , the remainder boiling at  $145^{\circ}$  to  $153^{\circ}$ . There was no substance boiling at a higher temperature.

"The first substance possessed the composition and properties of isoprene mono-hydrochloride,  $C_{10}H_8HCl$ .

"The second product, boiling at  $145^{\circ}$  to  $153^{\circ}$ , possessed the composition of a dihydrochloride of isoprene,  $C_{10}H_8.2HCl$ .

"The last product of the action of the acid upon isoprene is non-volatile (fixed). After this substance is treated for a long time with boiling water in order to free it from chlorine-containing substances, which accompany it, and which it obstinately retains, it has the percentage composition of isoprene. It contains little more than one part per hundred of chlorine, which may be due to the fact that it retains some of the volatile chlorinated compounds, or it may be due to the fact that the compound itself combines partially with hydrochloric gas ( $C = 87.1$ ;  $H = 11.7$ ;  $Cl = 1.7$ ). Furthermore, it possesses the elasticity and other characteristics of rubber itself. It is insoluble in alcohol; it swells up in ether, also in carbon disulfide in which it dissolves in the manner of natural rubber. When the product is submitted to dry distillation, it forms the same volatile hydrocarbons as rubber; I have isolated from these distillation products a certain quantity of a hydrocarbon,  $C_{20}H_{16}$ , which, when treated with hydrochloric acid, gave me the dihydrochloride,  $C_{20}H_{16}.2HCl$ , melting at  $+46^{\circ}$ , the same as the dihydrochloride from caoutchouc. This fact constitutes a new method for the synthesis of terpine (‘dipentene’) and of its derivatives, which was previously obtained only by the action of heat on isoprene. All of these properties appear to identify this polymer of isoprene with the substance from which isoprene is formed, namely, rubber. The quantity formed is notable and equals possibly one-sixth of the isoprene used."

There is, therefore, no doubt that Bouchardat actually claimed he had prepared an impure synthetic rubber in 1879, and it has frequently been stated that he was the discoverer of synthetic rubber.

It is to be remembered, however, that he obtained his isoprene by the dry distillation of natural rubber itself.

In June, 1911, Prof. Harries<sup>1</sup> made the following comment upon this work of Bouchardat:

"It was a bold idea of Bouchardat to directly connect isoprene with rubber, notwithstanding the fact that the dry distillation of rubber yields only extremely small amounts of isoprene." "I have ascertained that only 35 grams of the isoprene fraction, boiling at  $33^{\circ}$  to  $34^{\circ}$ , is obtained from  $1\frac{1}{2}$  kilograms of good rubber."<sup>2</sup> "I also regard it worthy of note that Bouchardat applied the term rubber to the mass resulting by the polymerization of isoprene, although he was deficient in practically all means of proving this statement experimentally. His experiments, as well as those of Tilden, have remained extremely incomplete."

However, I think it should be pointed out that Bouchardat gave an

<sup>1</sup> *Ann.*, 383, 184.

<sup>2</sup> *Gummi-Ztg.*, 24, 853 (March 18, 1910).

analysis of his product, stated that its elasticity and other properties were similar to those of rubber, mentioned its insolubility in alcohol, its behavior with ether, and its solubility in carbon disulfide as similar to that of natural rubber; and then he claimed to have submitted his product to dry distillation, and obtained the same volatile hydrocarbons as he had previously obtained from natural rubber.

In 1910 and 1911, Prof. Harries made use of the tetrabromides, the nitrosities and the ozonides as a means of identifying a sample of rubber. In 1912 and 1913, he finds that these tests are no longer suitable for the identification and comparison of the various rubbers, and he now says that the best method appears to be that of measuring the velocity of decomposition of the diozonides and dioxozonides with water, and the quantitative estimation of the decomposition products. In 1879, Bouchardat had naturally never heard of these tests for rubber, and we can hardly blame him for not employing them. He claimed to have used many of the best tests known at that time, and said he had synthetically prepared an impure rubber.

However, it is quite possible that Bouchardat was mistaken, and that the product which he claimed he had proved to be rubber, really should not be termed rubber at all.

Prof. Perkin, Jr. maintains that Bouchardat's product was an impure, but nevertheless a true rubber. However, Perkin, Jr. apparently relies wholly on Bouchardat's published work and its subsequent confirmation by Tilden. To the best of my knowledge, Perkin, Jr. has never stated that he has repeated Bouchardat's work and obtained true rubber by this method.

On the other hand, Prof. Harries maintains that he has been unable to confirm Bouchardat's work. In his paper<sup>1</sup> published on January 30, 1913, Harries says:

"Perkin again returns to the experiments of Bouchardat and Tilden, who claimed to have polymerized isoprene to rubber by means of hydrochloric acid gas, and he explains, contrary to my statements, that the observations of these investigators are undoubtedly correct.

"On different occasions I have pointed out that Bouchardat and Tilden, if they really did obtain rubber, must have accomplished this result purely by accident; for a large number of chemists have found it impossible to rediscover the conditions needed for the successful performance of this experiment. To those who are familiar with the property of rubber of energetically absorbing hydrochloric acid gas, the possibility of forming pure rubber by action of hydrochloric acid gas upon isoprene seems almost excluded; and further it would be impossible to manufacture a technically useful rubber by this method, because rubber containing hydrochloric acid is crisp or friable."

"Aside from this, I have in the past made numerous experiments in the attempt to polymerize isoprene to rubber by means of hydrochloric acid gas. The chief products of this reaction are always the chlorhydrines of isoprene. After the removal of these chlorhydrines by distillation with steam or by distillation in vacuum, there certainly remains a brown, tough residue. But this residue is for the most part soluble in alcohol, and the most important point is that when this residue is ozonized it

<sup>1</sup> *Ann.*, 395, 218.

never gives a test for levulinic aldehyde. I cannot relinquish the requirement that a product which is to be designated as true rubber, should at least be able to yield this qualitative test.

"If Mr. Perkin, Jr. is so much interested in the synthetic preparation of rubber by means of the action of hydrochloric acid gas on isoprene, I beg that he himself try at least once to rediscover the experimental conditions which were hidden by Bouchardat and Tilden. If then, Perkin can so describe the reaction that it may be successfully repeated every time, I will admit without reservation the priority<sup>1</sup> of Bouchardat and Tilden. At the present time I am not in a position to do so, although I appreciate thoroughly the work of these investigators, in so far as I recognize that they gave the hint or suggestion for the later results of Hofmann and myself."

This, at first, did not appear as convincing to me as it might, because every time Prof. Harries mentions this experiment, he speaks of acting upon isoprene with "*Salzsäuregas*," contrary to Bouchardat's description. Bouchardat never claimed to have prepared his rubber by the action of dry hydrochloric acid gas on isoprene; in fact he specifically says that this action does not yield rubber; he did use a solution of hydrochloric acid, made by saturating water at 0° with hydrogen chloride gas, and he states that this concentrated solution of hydrochloric acid acts differently upon isoprene than does dry hydrogen chloride gas.

Through the kindness of Mr. F. G. Achelis of The American Hard Rubber Co., I have been able to repeat this experiment described by Bouchardat. Mr. Achelis very generously supplied me with a suitable quantity of carefully washed and dried fine para rubber which was submitted to a dry distillation. The crude distillate has a rather disagreeable odor, due to the presence of certain volatile bases, which were removed by agitation of the oil with very dilute sulfuric acid, and then with water; the resulting oil was subsequently dried, and finally separated by repeated fractional distillation into several portions, the portion in which we are especially interested boiling at 33° to 60°. By careful and repeated rectifications over sodium, this was then separated into a chief fraction, boiling at 33° to 38°. From 7300 grams of the para rubber, I obtained 176 grams of this isoprene fraction. This fraction is, of course, an impure isoprene, pure isoprene,<sup>2</sup> regenerated from its dibromide by treatment with zinc dust, boiling at 33.5°.

Three portions of 25 grams each of this isoprene fraction were then treated in the cold in sealed pressure bottles with 300, 337.5 and 375 grams, respectively, of a solution of hydrochloric acid saturated at 0°. After agitation, they were allowed to remain at room temperature, one for 15 days, another for 17½ days, and the third for 20 days, thus corresponding with Bouchardat's directions, which state that "one part of isoprene was treated in the cold in a sealed vessel with 12 to 15 parts of the acid, and after agitation the whole was left at the room temperature for 15 to 20 days." No rise in temperature of the mixture, as noted by Bouchardat, was observed upon the first agitation. What might be termed a vigorous reaction took place immediately upon agitation, but

<sup>1</sup> See article by Harries in *Gummi-Ztg.*, 26, 1408 (June 7, 1912).

<sup>2</sup> Mokiewsky, *J. Russ. Phys. Chem. Soc.*, 30, 885; 32, 207.

this seemed to me due to rapid evolution of some of the hydrochloric acid gas from the saturated solution.

At the end of the reaction period, the contents of the bottles were added to water and submitted to distillation as long as oily drops were obtained. There remained, with the excess of acid water, only an extremely small, black, tarry residue, which was about as much as one would expect in a steam distillation of any impure oil.

This material was insoluble in alcohol, but readily soluble in ether. It might possibly be termed elastic, but would certainly *not* be called rubber, and it really is only a very inconsiderable residue. The volatile products resulting from the distillation were isoprene mono-hydrochloride and dihydrochloride, and these are certainly the *only* real products which I obtained by the method described by Bouchardat.

Accordingly, I can only say that I failed to successfully repeat Bouchardat's experiment, although I used every precaution to most carefully follow his directions. Personally, therefore, I believe that Prof. Harries and the chemists of Bayer & Co. are quite correct in maintaining that Bouchardat's priority can only be admitted with the reservation that no one since Bouchardat and Tilden has been able to successfully repeat this synthesis, and that it is really important for Prof. Perkin, Jr. or some one else to so describe Bouchardat's experiment that it may be readily and successfully repeated without involving a large amount of research.

In this connection it should be mentioned that Kondakow has offered a possible explanation of these contradictory results of the various investigators on the Bouchardat synthesis. Kondakow suggests that those chemists who have been unable to confirm Bouchardat's work have used freshly distilled isoprene (and that is certainly true in my own work), and that such isoprene does not give rubber when treated with hydrochloric acid. On the other hand, Bouchardat and Tilden, who claimed to have obtained rubber by treating isoprene with hydrochloric acid, may have used an isoprene which had stood for a long time in the light, and therefore contained more or less of rubber or rubber-like substance dissolved in it. On treating this solution of rubber or a rubber-like substance in isoprene with hydrochloric acid, Bouchardat and Tilden separated the rubber-like substance, and supposed that it had resulted from the action of the hydrochloric acid on the isoprene, whereas as a matter of fact it had been formed by the spontaneous polymerization of the isoprene on standing, before hydrochloric acid was added. Later work by Tilden, Weber, Wallach, and Pickles shows that isoprene on standing is converted slowly (nine months to eight years) into a rubber or rubber-like substance.

If this explanation should prove to be correct, then it might be argued that anyone from Williams in 1860 to the present time, who had made isoprene and allowed it to stand for some time, had unconsciously performed a synthesis of rubber or rubber-like substance, and the latter remained dissolved and unnoticed in the isoprene. Such an assumption might seem to warrant Prof. Perkin, Jr.'s statements that Williams' (1860) product "*undoubtedly contained rubber,*" that Bouchardat's product in 1875 "*contained a considerable proportion of rubber,*" and that Tilden's product made in 1884 by the action of cold acids on colophene, which resulted by the heating of isoprene at 250° to 280° for twelve hours,

contained rubber. Such an assumption, however, seems to me rather weak to base such positive statements upon, and is in reality "quite beside the mark."

The next work on synthetic rubber to be considered is that by Tilden, and around this has been waged a rather strenuous debate relative to the amount of credit due to Tilden as a discoverer of synthetic rubber, and as to how far his work anticipated the more recent developments, especially the work of Prof. Harries and of Bayer & Co.

In 1882, Prof. Tilden<sup>1</sup> presented a paper to the Southampton meeting of the British Association, on "Hydrocarbons of Formula  $(C_5H_8)_n$ ." He states:

"Isoprene is said to boil at  $37^\circ$  to  $38^\circ$ , though, according to my own observations, its boiling point is about  $3^\circ$  lower."

"Isoprene presents two characters which distinguish it from the terpenes. One is the peculiar explosive property of the white syrupy substance, which results from its oxidation by air. The other peculiarity—its conversion into true india-rubber or caoutchouc when brought into contact with certain chemical agents, for example, strong aqueous hydrochloric acid as noted by Bouchardat, or nitrosyl-chloride as observed by myself. It is this character of isoprene which gives it a somewhat practical interest, for if it were possible to obtain this hydrocarbon from some other and more accessible source, the synthetical production of india-rubber could be accomplished."

"When turpentine is passed through a red-hot iron tube and the product fractionally distilled, a small quantity of a liquid is actually obtained, having the same composition and some of the properties of isoprene. It boils at about  $37^\circ$ . By the action of concentrated hydrochloric acid it yields a tough substance closely resembling caoutchouc. The small quantity at present in my possession does not enable me to pronounce positively that this liquid is isoprene, but it seems very probable. A liter of turpentine gave about 20 cc. of the fraction from  $37^\circ$  to  $40^\circ$ , or thereabouts. I am engaged in the preparation of a larger quantity, and in the investigation of the somewhat complex series of hydrocarbons which are formed at the same time."

"I incline to the belief that it (isoprene) is  $\beta$ -methylcrotonylene."

The new facts announced in this paper are: (1) Isoprene boils at  $34^\circ$  to  $35^\circ$ . (2) By suitable treatment of turpentine, a 2% yield of a liquid resembling isoprene is obtained. (3) Tilden claims to have prepared true india-rubber by the action of nitrosyl-chloride on isoprene; but no details are given by means of which another chemist could readily confirm his results, and no analyses or properties of the product are mentioned, which would indicate to one reading the paper that this product really was a true rubber. To the best of my knowledge no other investigator has since confirmed this work, and I think that confirmation is desirable and necessary before we can accept it as a scientific fact that true rubber is made by acting on isoprene with nitrosyl-chloride. (4) Tilden claims to have prepared "a tough substance closely resembling rubber by the action of concentrated hydrochloric acid" upon synthetic isoprene. This is apparently a confirmation and development of Bouchardat's work, inasmuch as the latter used isoprene made from rubber it-

<sup>1</sup> *Chem. News*, 46, 220.

self, while Tilden used isoprene made from turpentine. No description of the process or properties of the product are given, hence it is impossible for a reader of the paper to say definitely that Tilden's product was real synthetic rubber.

Prof. Perkin, Jr., characterizes the above paper as "a remarkable tribute to Tilden's intuition that he should not only at this early date have foreseen the successful production of synthetic rubber, but he should also, at the same time, have suggested the correct formula for isoprene."

In 1884, Prof. Tilden published a paper<sup>1</sup> "On the Decomposition of Terpenes by Heat." He states:

"The following is a summary of the results of the examination of the products of the action of heat upon ordinary turpentine oil. 4000 cc. turpentine oil gave 380 cc. of a fraction boiling at 20° to 70°, which yielded about 200 cc. nearly pure pentene." "This liquid boils between 33° and 37°, and smells like isoprene, the pentene from india-rubber." "The formula,  $C_5H_8$ , is adopted for this liquid for reasons given hereafter, notwithstanding that the analytical numbers agree with the calculated percentages less closely than could be desired." "Conclusive proof of its composition was obtained by an examination of the polymerisation of this hydrocarbon by heat. A quantity of the fraction 33-35° was sealed up in tubes and heated at 250-280° for about twelve hours. No gas was evolved, but the liquid acquired a slight fluorescence. When submitted to distillation, a quantity of hydrocarbon apparently unaltered was recovered, but about half the volume distilled between 170° and 180°, while a small quantity of pale viscid colophene remained behind." The liquid boiling at 170° to 180° is shown to be dipentene, and is identical with the compounds previously described as diisoprene and terpine.

"In all probability, also, the pentene from turpentine is identical with isoprene. I have carefully compared them together, and cannot observe any essential difference between them." "Both hydrocarbons absorb hydrochloric acid gas eagerly, giving a mixture of monochloride and dichloride."

"Bouchardat mentions that the action of concentrated hydrochloric acid upon isoprene converts a portion of the hydrocarbon into caoutchouc. This substance is also formed from the turpentine hydrocarbon. It appears to be produced most readily from the oily polymeride, resulting from the action of heat. Contact with strong acids in the cold effects the change." "The pentene obtained from the terpenes is identical with isoprene. This pentene is readily polymerised by heat into terpine,  $2C_5H_8 = C_{10}H_{16}$ ."

An analysis of this paper shows the following facts:

(1) Turpentine is "cracked" into isoprene by the action of heat, the yield of nearly pure isoprene being about 5% of the volume of turpentine employed. (2) Caoutchouc is said to be formed from this isoprene obtained from turpentine (presumably by the action of concentrated hydrochloric acid upon the isoprene). (3) No analysis or description or properties of this alleged caoutchouc are given. (4) The formation of this caoutchouc was one of the methods used to prove that the isoprene from turpentine was identical with the isoprene formed by the dry distillation



of rubber. (5) When this isoprene obtained from turpentine is heated in sealed tubes for 12 hours at  $250^{\circ}$  to  $280^{\circ}$ , about one-half of it is converted into terpineol or dipentene, a small quantity is polymerized to "pale viscid colophene," and the remainder is unaltered. (6) Tilden claims that rubber "appears to be produced most readily from the 'oily polymeride,' resulting from the action of heat on isoprene. Contact with strong acids in the cold effects the change."

What does Tilden mean by this "oily polymeride?" Certainly not the unchanged isoprene, hardly the dipentene boiling at  $170^{\circ}$  to  $180^{\circ}$ , and therefore it must be the "*pale viscid colophene*." Accordingly, Tilden claims to have synthetically prepared rubber by bringing colophene in contact with strong acids *in the cold*. It seems almost impossible. However, we must bear in mind that Prof. Perkin, Jr. says there is no doubt that the colophene made by Bouchardat in 1875 by heating isoprene in sealed tubes at  $280$ – $290^{\circ}$  "contained a considerable proportion of rubber," and therefore Tilden's colophene made in a similar manner might be expected to contain rubber, even before it came in contact with cold acids. Moreover, in referring to this paper, Prof. Perkin, Jr. says:

"In confirmation of Tilden's results, Lilley, by heating isoprene, recently obtained a body which he called 'mesoprene' (clearly Tilden's 'oily polymer'), and showed that this may be converted into rubber by the action of acid or other agents." And again Perkin remarks:

"On December 14, 1909, G. Lilley, working in England, took out the patent<sup>1</sup> to which I have already referred for making 'mesoprene' by the action of heat on isoprene, and then acting upon the oily polymeride thus formed, with acids, etc. We have seen samples of the rubber made in this way and their formation by this process completely vindicates Tilden's early statements, if such vindication were necessary."

The Lilley patent, cited by Perkin, Jr. in confirmation and vindication of Tilden's statement, is on "The Production of Synthetic India-Rubber or Rubber-like Material." It states:

"'Mesoprene' is the name given to a product obtained by heating the 'basic principle of india-rubber' or a body containing the same at a temperature below  $200^{\circ}$  under pressure, either alone or in presence of some added substance or substances, such as (1) mesoprene, (2) alcohol, or other rubber precipitant, (3) a liquid hydrocarbon mixture, obtained as a by-product in the production of mesoprene, (4) an acid. The 'basic principle' may be treated with air or oxygen before subjecting it to the action of heat. Any unconverted substance is removed by distillation, the residue in the still constituting mesoprene, which is free from water by drying *in vacuo* at  $100^{\circ}$ . The distillate, or a portion of it, constitutes the liquid hydrocarbon mixture referred to under (3) above. The 'basic principle of india-rubber' is obtained by subjecting the vapour of turpentine or a selected fraction or fractions of the distillates from the crude turpentine exudation to a temperature of about  $500$ – $600^{\circ}$ , condensing the products and separating the more volatile constituents by fractionation, preferably selecting the portions distilling below  $90^{\circ}$ , in which isoprene and other hydrocarbons suitable for the purpose of the invention are present.

<sup>1</sup> Eng. Patent, 29,277. Date of application Dec. 14, 1909; accepted Mar. 14, 1911; *J. Soc. Chem. Ind.*, 30, 561; *C. A.*, 5, 3173 (1911).

"The synthetic india-rubber, or rubber-like body, is produced by heating 'mesoprene,' prepared as above described, either alone, or by floating it on water heated to 100°, or in the presence of sulfuric acid or its decomposition products, or hydrochloric acid, or sulfur dioxide which may be passed through the dry heated mesoprene."

This is a very interesting patent in some respects, but I still fail to see how it vindicates or confirms Tilden's statement that "*contact with strong acids in the cold effects the change*" of colophene (made by heating isoprene at 250–280°) into rubber. For so-called "mesoprene," *made by heating oxidized or ozonized isoprene and other hydrocarbons suitable for the purpose at a temperature below 200°, with alcohol and an acid,* is not necessarily the same as colophene made by heating isoprene alone at a temperature of 250° to 280°.

Therefore, I believe Tilden's statement—that the contact of pale, viscid colophene with strong acids in the cold, produces rubber—needs accurate confirmation. As a matter of fact, later statements<sup>1</sup> made by Tilden in 1906 and 1908 show that when he tried to make rubber from isoprene "by heat or contact with strong reagents, the greater part of the hydrocarbon is converted into dipentene and the mixture of viscid compounds of high boiling point known as colophene, which results from the polymerisation of the terpenes." There is no intimation that the strong reagents then converted this colophene into rubber.

In this connection, and bearing direct testimony upon the question as to whether colophene does or does not contain rubber, it is interesting to again quote from Harries' recent paper.<sup>2</sup> He says:

"While engaged with the problem of the conversion of isoprene into rubber, I made many experiments to bring about the polymerisation of this hydrocarbon by means of catalytic agents. The resulting product was then always at first ozonized to see whether it gave the pyrrol test. The results showed that most of the oils and resins (colophene), which were obtained, did not give this test, and therefore had nothing to do with rubber."

Again referring to this paper by Tilden, Prof. Perkin, Jr. says: "This paper is of special interest since we have here the first possibility of the commercial manufacture of rubber."

In 1908, Tilden is reported as saying, relative to the commercial manufacture of rubber from isoprene made from turpentine:

"If isoprene were obtainable at a low cost from other sources, it might be found possible to utilize the hydrochloric acid process, though I doubt it."

And again on December 11, 1912, in the discussion of Dr. F. M. Perkin's lecture, Sir William Tilden said:

"The key to synthetic rubber was provided by the discovery made by Dr. Matthews, of the remarkable action of the metal sodium. Without some such method for rapidly producing polymerisation it would be impracticable with the amount of isoprene, or other hydrocarbon, to come within measurable distance of producing rubber for practical purposes."

<sup>1</sup> Report of the British Association for the Advancement of Science, 1906, York. Transactions of Section B, page 525.

<sup>2</sup> *Ann.*, 395, 220.

In his second paper<sup>1</sup> "On the Terpenes," dated December 19, 1884, Wallach refers to the heat polymerisation of the isoprene obtained by the dry distillation of rubber, with these words:

"Isoprene has recently been investigated by Bouchardat and Tilden with very interesting results. Both agree that on heating, isoprene is polymerized to a hydrocarbon,  $C_{10}H_{16}$ , which is identical with caoutchine. *I can confirm these statements in every respect.*

"When isoprene is heated for some hours at  $250^{\circ}$  to  $270^{\circ}$ , there is formed, together with high boiling polymerization-products, a hydrocarbon boiling at  $180^{\circ}$ , which has been identified by its tetrabromide as caoutchouc or di-isoprene, and this is identical with cinene."

In 1886 Wallach<sup>2</sup> tried various methods for the polymerisation of the isoprene obtained by the distillation of rubber. He mentions incidentally:

"When isoprene is placed in sealed tubes and is exposed to the action of light for a long time, a product is formed which, when treated with alcohol, forms a tough mass, resembling rubber; this material became more or less hard on exposure to air."

Nothing more is said about this product.

On May 18, 1892, Prof. Tilden read a paper<sup>3</sup> before the Philosophical Society of Birmingham on "The Spontaneous Conversion of Isoprene into Caoutchouc." I quote the following from this paper:

"Bouchardat observed that when isoprene is heated to a temperature near  $300^{\circ}$ , it gradually polymerises into a terpene which he called di-isoprene, but which is now usually called *dipentene*. This compound boils at  $176^{\circ}$ . A quantity of colophene similar to that which is produced by the action of heat upon turpentine is formed at the same time.

"When isoprene is brought into contact with strong acids, aqueous hydrochloric acid for example, it is converted into a tough elastic solid, which has been examined by G. Bouchardat and by myself; it appears to be true india-rubber.

"Specimens of isoprene were made from several terpenes in the course of my work on those compounds, and some of them I have preserved. I was surprised a few weeks ago at finding the contents of the bottles containing isoprene from turpentine entirely changed in appearance. In place of a limpid colourless liquid the bottle contained a dense syrup, in which was floating several large masses of solid of a yellowish colour. Upon examination this turned out to be india-rubber. The change of isoprene by spontaneous polymerisation has not to my knowledge been observed before. I can only account for it by the hypothesis that a small quantity of acetic or formic acid had been produced by the oxidising action of the air, and that the presence of this compound had been the means of transforming the rest. The liquid was acid to test paper, and yielded a small portion of unchanged isoprene.

"Synthetic india-rubber, like natural rubber appears to consist of two substances, one of which is more soluble in benzene or in carbon bisulphide than the other. A solution of the artificial rubber in benzene leaves on evaporation a residue which agrees in all characters with a similar preparation from para rubber. The artificial rubber unites with

<sup>1</sup> *Ann.*, 227, 295.

<sup>2</sup> *Ibid.*, 238, 88.

<sup>3</sup> *Chem. News*, 65, 265 (1892).

sulphur in the same way as ordinary rubber, forming a tough elastic compound.

"The constitutional formula of isoprene is not known with certainty, but it must be selected from the five following formulae." Three of these formulas represent derivatives of allene, and two are derived from crotonylene.

"It is obvious that compounds such as these containing doubly-linked carbon may polymerise in a variety of ways, and in the present condition of our knowledge of the constitution, even, of isoprene, it would be idle to speculate as to which one of the numerous possible arrangements would correspond to the constitution of caoutchouc."

The important facts presented in this paper are: (1) Heat polymerizes isoprene to dipentene and colophene, the latter being similar to that formed by the action of heat on turpentine. (2) Tilden confirms Bouchardat's work on the conversion of isoprene into a tough elastic solid, which appeared to be true india-rubber, by the action of aqueous hydrochloric acid; no description of the product is given. (3) The spontaneous polymerization of isoprene into rubber or a rubber-like substance in the course of eight years is noted. (4) Some properties of this synthetic rubber are given, such as its solubility in benzene and carbon disulfide, its color, elasticity, and the fact, that it combines with sulfur like natural rubber. This is noteworthy, because in his papers on the polymerization of isoprene to rubber-like substances, Tilden rarely gives much information regarding the properties of his products.

This important discovery by Tilden of the spontaneous polymerization of isoprene to rubber, or a rubber-like substance, was soon corroborated by Dr. C. O. Weber, and some eighteen years later was confirmed by S. S. Pickles. Therefore, to Tilden belongs the entire credit of having prepared rubber, or a product closely resembling rubber, for the first time, by the slow spontaneous polymerization of synthetic isoprene, and he apparently had synthetic rubber, or something very similar to it, in his hands as early as 1892.

Regarding Tilden's previous work on rubber, I think we shall have to agree with Prof. Harries when he remarks that Tilden's experiments on rubber were certainly *extremely incomplete*.

A paper<sup>1</sup> of interest and importance in this case, and one which bears direct testimony regarding Tilden's synthesis of rubber in 1892 by the slow polymerization of isoprene, was read by C. O. Weber before the Manchester Section of the Society of Chemical Industry, on January 5, 1894.

I quote the following from this paper:

"Tilden obtained isoprene by distilling turpentine through porcelain tubes at a dull red heat, and discovered subsequently that this compound, on standing, spontaneously polymerises into india-rubber. I am in a position to confirm this observation with respect to isoprene obtained from india-rubber by dry distillation. About 300 grams of this substance were found after nine months' standing to be converted into a very viscid, treacly mass, from which by treatment with methyl alcohol, a solid spongy substance of almost white colour could be separated. This substance, after drying, was of a light brown color, and in all respects identical with

*J. Soc. Chem. Ind.*, 13, 11 (1894).

india-rubber. The weight of india-rubber thus obtained was 211 grams.

"Whether in the future we shall succeed to manufacture india-rubber artificially by means of isoprene appears very doubtful as yet. The manufacture of cheap isoprene is certainly an exceedingly difficult task to start with, and on the other hand we have not succeeded so far to completely polymerise it into india-rubber. The by-products of this polymerisation consist of dipentene and polyterpenes, which will always remain comparatively worthless, there being any amount of cheap natural terpenes. At the present time the constitution of isoprene itself is very doubtful."

Regarding the constitution of rubber, Weber says:

"All these condensation products of isoprene are terpenes or polyterpenes, and the fact that the results of the analysis of india-rubber lead to the empirical formula,  $C_{10}H_{16}$ , which is that of the terpenes, might induce us to pronounce also india-rubber a terpene, or possibly a polyterpene  $(C_{10}H_{16})_n$ . What we know with certainty is the formation of india-rubber from isoprene by polymerization, and we further know that the molecular weight of it is much higher than  $C_{10}H_{16}$ . Under these circumstances it appears very much preferable to describe india-rubber as a polyprene  $(C_5H_8)_n$ ."

In this paper, Weber gives the yield of his product, stating that he obtained a little more than two-thirds of the weight of the isoprene used. He also gives the time required to accomplish the spontaneous polymerization of isoprene to his rubber, *viz.*, nine months; this seems like an extremely short time, for the testimony of other investigators is that it requires several years to accomplish this spontaneous change. Thus, judging by the dates of Tilden's papers, he found the change to have taken place after seven or eight years. In a more recent article, Pickles states that when isoprene is allowed to stand for  $3\frac{1}{2}$  years it is only incompletely converted into an immature rubber. Hence, Weber must have happened upon conditions which were not met with by the others.

Unfortunately, Weber gives no analyses or specific properties by which he identified his synthetic rubber; he simply states that his product was "in all respects identical with india-rubber," and some will agree that he was qualified to know about it, and will accept his word that he had synthetic rubber in his hands prior to the year 1894. Others will be within their rights and can scarcely be regarded as unreasonable, if they maintain that Weber may possibly have prepared a rubber-like substance, but that he gave no proof which can be regarded as establishing as a scientific fact that he actually prepared synthetic india-rubber.

In 1910, S. S. Pickles published a paper<sup>1</sup> on "The Constitution and Synthesis of Caoutchouc" in which he confirms Tilden's and Weber's spontaneous polymerization synthesis. Under the heading "Spontaneous Polymerisation of Isoprene and Examination of the Product," Pickle says:

"In view of the position of the subject at the present time, the author considered that an account of the result of a recent experiment on the polymerisation of isoprene might have some little value, especially as chemical tests were applied to the product obtained. The difficulty so far as repetition is concerned lies in the fact that the process of spon-

<sup>1</sup> *J. Chem. Soc.*, 97, 1086 (1910).

taneous polymerisation is an extremely slow one, the complete conversion requiring several years.

"In 1906, the author prepared a specimen of isoprene (about 10 grams for demonstration purposes), from plantation biscuit rubber; it boiled at 35° to 37°. The small bottle containing it was almost full, the stopper was securely fastened down, and the specimen was allowed to remain in that condition (for the greater part of the time in the dark) for three and a half years. The liquid, which at first was as mobile as ether, had, during this period, gradually become more viscous, until it acquired the consistency of a thick syrup. A short time ago a portion of this liquid was poured out, and to it was added about 10 volumes of alcohol. The separation of a white substance, followed by a clotting, took place immediately. The coagulum thus formed was washed with alcohol and allowed to dry on a glass plate. As thus prepared, the material was clear, gelatinous, and possessed of a certain amount of elasticity. In point of tenacity however, it was certainly not equal to mature Para rubber, but rather resembled the product obtained from young, immature rubber trees. It should be remembered, however, that in the experiment the polymerisation had not been allowed to proceed to completion, that is, until reaching the completely solid state. That the material undoubtedly contains rubber, however, is proved by the fact that it yields the characteristic tetrabronide and the nitrosite."

This would seem to unquestionably confirm Tilden's synthesis of rubber by the slow spontaneous polymerization of isoprene, and prove that he had a true synthetic rubber in 1892.

However, in his last paper<sup>1</sup> on this subject, Prof. Harries describes certain investigations on the rubber-like products obtained from  $\beta,\gamma$ -, or 2,3-dimethylbutadiene, which seem pertinent at this point. He finds that the normal dimethylbutadiene rubber, prepared according to the Elberfeld method of heating dimethylbutadiene for some time in closed tubes, and the white, solid, practically insoluble mass, which Kondakow obtained by allowing dimethylbutadiene to stand in closed tubes for about a year at the ordinary temperature, are different in physical and chemical properties. In this connection Harries says:

"The product obtained by polymerizing dimethylbutadiene at elevated temperatures is apparently different from the product obtained by its slow, spontaneous polymerization in the cold; the latter is absolutely not a true rubber. The determination of this fact appears to me of great importance, because it naturally follows from this that isoprene, and the butadiene hydrocarbons in general, will yield a different product by the slow, spontaneous polymerization in the cold, than by the polymerization at elevated temperatures. Hence, the proof recently advanced by Pickles,<sup>2</sup> that isoprene is converted into rubber by long standing in the cold, is uncertain, because the products of cold polymerization also yield bromides and nitrosites which are difficult to distinguish from those obtained from the heat-polymerization products.

"In order to study this question somewhat more closely, I placed some pure isoprene in a quartz-glass tube, sealed it, and exposed it to the action of the ultraviolet rays for 20 days and nights. At the end of this

<sup>1</sup> *Ann.*, 395, 265.

<sup>2</sup> *J. Chem. Soc.*, 97, 1085 (1910).

time, I obtained a white, solid product, which possesses great similarity with the product obtained by Kondakow by the cold polymerization of dimethylbutadiene. This product is tough at first, later becoming brittle, and is absolutely insoluble. Together with this insoluble product, there was formed a small amount of a rubber-like substance, which in my opinion was formed by the unavoidable heating of the isoprene by the lighting process. Unfortunately the quantities of the substances formed were too small to permit of closer investigation."

This, then, appears to reopen the question, does the slow, spontaneous polymerization of isoprene at ordinary temperatures produce a true rubber? Tilden, Weber, Pickles, and Perkin, Jr. are on record in the affirmative; Harries inclines to the negative.

At a meeting of the British Association for the Advancement of Science held at York in 1906, Prof. Tilden submitted a paper<sup>1</sup> "On the Polymerisation of Isoprene." He says:

"When kept for a long time isoprene is slowly converted into india-rubber, the process, however, occupying many years. The specimens now exhibited illustrate the process of transformation. If any attempt is made to hasten the operation, as by heat or contact with strong reagents, the greater part of the hydrocarbon is converted into dipentene, and the mixture of viscid compounds of high boiling-point known as colophene, which results from the polymerisation of the terpenes."

The next important reference concerning Prof. Tilden's work on synthetic rubber is found in the *India-Rubber Journal*,<sup>2</sup> published in the year 1908. I quote the following from an article in this Journal:

"In a letter once published in the 'Kew Bulletin,' the learned and enthusiastic Professor (Tilden) stated that: 'As you may imagine I have tried everything I can think of as likely to promote this change (of isoprene into rubber), but without success. The polymerisation proceeds *very slowly*, occupying according to *my experiences several years*, and all attempts to hurry it result in the production, not of rubber, but of colophene, a thick, sticky oil, quite useless for all purposes to which rubber is applied.'"

Statement for *India-Rubber Journal* readers:

"Professor Tilden has courteously sent in the following letter which embodies the result of his researches up to date, and his opinion of the future possibilities of synthetic rubber, for publication in the 'India-Rubber Journal.' We have not yet met a manufacturer (and we never expect to meet a planter) who hails the possible advent of a commercial synthetic rubber with any symptoms of joy; the Professor's letter will therefore be followed with unmixed pleasure by our readers. He writes:

" 'The conversion of isoprene into rubber occurs, so far as observed, under two conditions: (1) When brought into contact with strong aqueous hydrochloric acid or moist hydrogen chloride gas; (2) by spontaneous polymerisation. In the former case the amount of rubber produced is small, as it is only a by-product attending the formation of the isoprene hydrochlorides which are both liquids. *In the latter case the process oc-*

<sup>1</sup> Report of the British Association for the Advancement of Science, 1906, York. Transactions of Section B, page 525.

<sup>2</sup> *India-Rubber J.*, 36, 321-322 (1908); *Gummi-Zig.*, 23, 151 (Nov. 6, 1908); see also *Ann.*, 383, 185; "Die Synthese der Kautschuks," by Ditmar, page 24.

*cupies several years.* Of course, many attempts were made by me to hasten the process, but it was found that contact with any strong reagent, such as oil of vitriol, pentachloride of phosphorus, and others of milder character, led only to the production of a sticky colophene similar to the substance which results from the polymerisation of the terpenes, and after a course of experiments which were carried on for about two years, I was reluctantly obliged to abandon the subject. *It is, however, a question whether the process could be made commercially productive even if a suitable reagent could be found to effect the transformation, because the yield of isoprene from turpentine is very small, probably not exceeding 10% under favorable conditions. In my experiments it was less. If isoprene was obtainable at a low cost from other sources it might be found possible to utilize the hydrochloric acid process, though I doubt it.*"

No better summary of Prof. Tilden's work on synthetic rubber could be given than he himself gives in this article, published a few years before the controversy regarding his work commenced. It is interesting to note that he makes no claim that his colophene contained a "considerable proportion of rubber," or that cold acids converted this "oily polymeride" into rubber. It is needless to say that this article by Tilden does not fit in any too well with Prof. Perkin's argument, and in his paper of 1912 in the *Journal of the Society of Chemical Industry* he omits all reference to it. It is likewise apparent that this statement by Tilden pleases the German investigators and they quote it.

This brings us up to the year 1909, the date of the first patents of Bayer & Co., Elberfeld, on the heat polymerisation of isoprene and of other butadiene hydrocarbons to synthetic rubbers.

For the sake of a clear understanding of some subsequent developments, I desire to quote certain portions of Bayer & Co.'s first German patent application,<sup>1</sup> dated September 11, 1909, on "A Method for the Preparation of Artificial Rubber." The patent says:

"An observation of exceedingly great importance technically has been made in the discovery of the fact that by heating synthetic isoprene, a very good yield of a product is obtained, which, in its chemical and physical properties, cannot be distinguished from natural rubber."

"With our process, the temperature may vary within fairly wide limits, but if it greatly exceeds 200° large amounts of terpenes are readily formed. In carrying out the reaction, the synthetic isoprene may be heated in the presence of indifferent diluting agents or solvents, or in the presence of neutral, alkaline or acid catalysts.

"Example 1. 200 parts of isoprene are heated in an autoclave at 200° for 10-12 hours, when a very tough and elastic, but sticky mass is formed. The stickiness is removed by passing steam through the mass, and there results a substance which cannot be distinguished from natural rubber.

"Example 2. 500 parts of isoprene are warmed in a pressure-vessel at 90-100° for six days. The resulting viscous mass is then distilled with steam at ordinary pressure until all unchanged isoprene is driven over. Then, the steam distillation is continued under diminished pressure until no more oil comes over. On cooling, a pure, white rubber of excellent quality remains in the distillation apparatus.

<sup>1</sup> Deutsche Patentanmeldung F. 28390, Kl. 39 b. Gr. 1, vom 11, Sept., 1909. Von den Farbenfabriken vorm. Friedr. Bayer & Co., Elberfeld.



"Example 3. 100 parts of isoprene are dissolved in 200 parts of benzene, and the solution is heated under pressure at 120° for two days; the product is then distilled, first at ordinary pressure and finally in vacuum. Unaltered isoprene, benzene, and terpenes pass over first, and a tough, transparent mass remains, which, after washing with alcohol, loses its transparency, and assumes the outward appearance of rubber.

"*Patent Claim.* A process for the preparation of artificial rubber, which consists in heating synthetic isoprene, with or without the addition of agents promoting polymerisation, at a temperature under 250°."

In his address before the London section of the Society of Chemical Industry on June 17, 1912, Professor Perkin, Jr., says:

"I should like next to call attention to a German application (H44,823) lodged in October, 1908, by A. Heinemann, but apparently not published until September, 1911. This patent (corresponding to the English patent, 21,772/07; see THIS JOURNAL, 1908, 1075) describes the method of heat polymerisation of isoprene as follows:

"This hydrocarbon contains two double bonds and so is easily polymerised. This follows in known manner by heating in a sealed tube with or without the addition of acids, alkalis or neutral catalysts. The temperature is preferably kept at 100° to 150° for three days. Higher or lower temperatures work in a shorter or longer time than three days. After polymerisation, a rubber-like mass is obtained, in solution in unpolymerised hydrocarbon or hydrocarbon polymerised only to an oil. The hydrocarbon can be separated by distillation or by the known methods of precipitating natural rubber."

Perkin, Jr., continues as follows: "Meanwhile, the Bayer & Co. had been at work on the problem and filed an English patent, 17,734/10 (see THIS JOURNAL, 1911, 226), dated September 11, 1909, and a French patent, 419,316, the first of a series of patents for the heat polymerisation of isoprene and its homologues. The gist of these patents is very well described by Heinemann's remarks, which I have just quoted, and they do not appear to contain much which was not known before."

If Perkin's statements are correct and his conclusion is justified, then we are allowed to infer that the chemists of Bayer & Co., by some strange coincidence, applied for a patent, in which they described their discovery in nearly the same language which Heinemann had one year previously used in a patent application to describe the same discovery. If Perkin's statements were based upon insufficient information, and the facts are not as he stated, then, it seems to me, an injustice has been committed against the chemists of Bayer & Co.

In a short article<sup>1</sup> in "Gummi-Zeitung," for August 9, 1912, Dr. Fritz Hofmann, of Elberfeld, replies to this statement by Perkin, Jr., in the following words:

"The Heinemann application H44,823 was definitely or finally rejected by the German patent office in May, 1912. This application as a matter of fact did contain the parts quoted by Perkin, but these particular parts were never contained in the original application filed in October, 1908. Furthermore, the parts quoted by Perkin are not contained in Heinemann's English patent, 21,772/07, nor are they to be found in

<sup>1</sup> *Gummi-Ztg.*, 45, 1794 (1912). See also *Ibid.*, 26, 1458 (June 14, 1912); 26, 1752 (Aug. 2, 1912).

Heinemann's French patent, 394,795. In the German application, H44,823, the part quoted by Perkin was first introduced as an addition on December 14, 1910, that is, at a time when the heat polymerisation of isoprene had become generally known through the well-known Vienna lecture of Prof. Harries on March 12, 1910, and by the French application of the Badische Anilin- und Sodafabrik—made public on November 8, 1910. The basic patent of the Farbenfabriken vorm. Friedr. Bayer & Co., which for the first time described the heat polymerization and patented this discovery, was delivered at the Imperial patent office on September 11, 1909."

On investigation, I find the facts relative to Heinemann's English patent, No. 21,772, which Perkin, Jr., mentions as corresponding with the German application, are as follows:

Date of application, October 2, 1907. Accepted October 1, 1908. Subject, "A Process for the Synthetic Production of India-Rubber," by Arthur Heinemann of London. The discovery is given as follows: "Acetylene and ethylene are mixed together and heated in a tube or the like raised to a dull red heat, thus producing divinyl. The divinyl is then converted into methyl divinyl or isoprene in any well-known manner, such for instance, as by the action of methyl chloride, or by passing the three gases together through said tube. The methyl divinyl or isoprene resulting from the last reaction is then treated with concentrated hydrochloric acid and condensed to caoutchouc."

"Caoutchouc prepared by the above described method is as good as the natural product, with which it can compete."

There is absolutely no reference in this patent to the heat polymerization of isoprene.

Heinemann's French application,<sup>1</sup> dated September 30, 1908, is exactly like the English patent and contains no reference to the heat polymerization of isoprene. These patents deal with an alleged process of preparing synthetic isoprene and then polymerizing this by Bouchardat's method.

The abstract in the *Journal of the Society of Chemical Industry* for 1908, to which Perkin, Jr., refers, gives a very short notice of Heinemann's English patent, saying that isoprene is formed from acetylene, ethylene and methyl chloride, and that the resulting isoprene is condensed to rubber; but absolutely no mention is made of the condensing or polymerizing agent, nor of heat polymerization.

Regarding Heinemann's German application, H44,823, dated October 1, 1908, I find this printed in Dr. Rudolf Ditmar's monograph on "The Synthesis of Rubber," the preface of which is dated March, 1912. As printed in this book, the German application includes the heat polymerization of isoprene as quoted by Perkin, Jr. If one used this book in this connection, there would be some reasons for believing that the German application, dated October 1, 1908, anticipated Bayer & Co.'s 1909 patent. However, in the part of the patent application relating to the polymerization of isoprene, as quoted by Perkin, Jr. there is one phrase which would be looked upon with *surprise*, at least, by those familiar with the history of synthetic rubber, and that is: The polymerization of isoprene to rubber "follows in *known manner* by heating in a sealed tube with or without the addition of acids, alkalies, or neutral catalysts."

<sup>1</sup> C. A., 4, 2746 (1910).

On October 1, 1908, the date Perkin, Jr., assumes this to have been presented to the German patent office, and indeed up to September 11, 1909, the *known methods* of polymerizing isoprene were: (1) Bouchardat's, Tilden's, and Wallach's experiments of heating isoprene in sealed tubes at 250° to 290°, when dipentene and a mixture of diterpenes termed colophene were formed, but no rubber was mentioned by these investigators. (2) Bouchardat's and Tilden's work in treating isoprene in the cold with strong aqueous hydrochloric acid, which gave a small yield of a product which they termed synthetic rubber. (3) Wallach's, Tilden's and Weber's experiments on the slow, spontaneous polymerization of isoprene at ordinary temperatures to a rubber-like product.

If this part in Heinemann's German application was really written prior to October 1, 1908, then Heinemann's process of heat polymerization of isoprene to rubber was a new discovery of great importance, and it is remarkable that he should term it a "*known method.*"

Furthermore, there is no reason to doubt Dr. Hofmann's word regarding this patent situation, and I think we are not warranted in assuming that the "gist" of the Bayer & Co. patent was described by Heinemann in 1908.

This brings us up to the time of the Bayer & Co. and Prof. Harries' patents and publications, and it may be regarded as the close of the first period in the history of synthetic rubber.

We may, therefore, summarize the pioneer work on the polymerization of *isoprene* to rubber, *i. e.*, the work published up to about September 11, 1909, as follows:

1. A synthetic rubber was first claimed by G. Bouchardat in 1879 by polymerization of isoprene in the cold by means of strong aqueous hydrochloric acid. This synthesis is said to have been confirmed by Tilden in 1882 and 1884, and by A. Heinemann in 1907. It has been denied by Professors Klages and Harries, and by Bayer & Co., and has been defended by Prof. Perkin, Jr., who has not, to my knowledge, stated that he himself ever made true rubber by this process.

(2) In 1882 and 1884, Professor Tilden claimed to have produced rubber by the action of nitrosyl-chloride on isoprene, and by the action of *cold acids* on the "oily polymeride," colophene, produced by heating isoprene at 250° to 280° for about twelve hours. To the best of my knowledge, neither of these syntheses has been confirmed by any other investigator.

(3) Bouchardat, in 1875, and Tilden and Wallach in 1884, all agreed that heating isoprene in sealed tubes at 250° to 290° for several hours, converted it into dipentene and colophene; the *formation of rubber under these conditions was not noted by these investigators.* Prof. Perkin, Jr. claims "there can be no doubt that this colophene contained a considerable proportion of rubber."

(4) In 1886, Wallach noted that when isoprene was exposed to the action of light for a long time, a tough mass, resembling rubber was formed. This product was apparently not further investigated.

(5) In 1892, Prof. Tilden discovered the spontaneous polymerization of isoprene to rubber or a rubber-like substance, the process requiring a number of years for its completion. This synthesis has been confirmed by Weber and Pickles, but the question as to whether this product should be regarded as a true rubber has been raised by Prof. Harries.

(6) On September 11, 1909, Bayer & Co. patented their first process for the preparation of artificial rubber, consisting in heating synthetic isoprene with or without the addition of neutral, alkaline, or acid catalysts, at a temperature under 250°. In my opinion, there is absolutely nothing in the prior state of the art, which can be regarded as anticipating this discovery of the chemists of Bayer & Co.

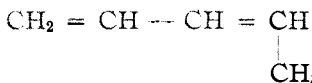
So far we have considered the early history of the polymerisation of isoprene only. A few words should be added regarding what was known to the earlier investigators about the polymerisation products of isomers and homologues of isoprene, because it has been intimated that the polymerides obtained from these substances, in their behavior with solvents and in certain of their properties, showed a general resemblance to the properties of rubber. It is also clear that those who call our attention to these polymerization products, permit us to infer that this alleged resemblance to rubber should, in some way, anticipate the work of Prof. Harries and Bayer & Co. But we should remember that this class of unsaturated compounds are readily polymerized or resinified; and we know that in working with organic compounds, we have obtained tarry or resinous products which we may have termed gummy or rubber-like, but which we never dreamed of having any real relationship with true india-rubber.

We will first consider *piperylene*, an isomer of isoprene. In 1881, Hofmann<sup>1</sup> examined piperylene. He says: "The boiling point of this substance is about 42°; towards the end of this distillation, the temperature rose somewhat, so that possibly the polymerization of a small amount may be indicated."

In 1882, Schotten<sup>2</sup> tried to prepare piperylene from nitro-piperidine. He says: "I have found that on heating with phosphoric anhydride, as well as with zinc chloride, only traces of piperylene are formed, and that the mass is largely resinified (verharzt)."

I mention the above two references because Prof. Perkin, Jr.<sup>3</sup> calls attention to these as indicating that Hofmann and Schotten "obtained similar polymerides," and that here "we find the first example of the polymerization of a homologue of isoprene."

In 1901, J. Thiele<sup>4</sup> published a paper on piperylene. I quote the following from this paper: "Piperylene has the constitution of an  $\alpha$ -methyl-butadiene,



"The boiling point of piperylene, in contrast to that of the  $\beta$ -methyl-butadiene (isoprene), is unchanged even after several months' standing in the dark, and as a residue there remains only a minimum amount of a gummy (gummiartigen) substance, probably a polymerisation product."

Prof. Perkin, Jr.<sup>3</sup> in using this reference says: "In 1901, Thiele showed that on keeping, it (piperylene) yielded a small quantity of a rubber like polymer, but not so readily as isoprene does."

<sup>1</sup> *Ber.*, 14, 665.

<sup>2</sup> *Ibid.*, 15, 425.

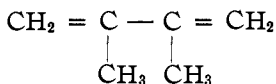
<sup>3</sup> *J. Soc. Chem. Ind.*, 31, 617.

<sup>4</sup> *Ann.*, 319, 227.

<sup>5</sup> *J. Soc. Chem. Ind.*, 31, 618.

We must keep in mind, however, that Thiele used the word "gummiartigen" and not "kautschukartigen."

Another compound to which our attention has been called is 2,3-dimethylbutadiene, or as it has frequently been termed, dipropylene or diisopropenyl,



In 1890, Marintza<sup>1</sup> stated: "Dimethyl isopropenyl carbinol was subjected to the action of sulfuric and hydrochloric acids. When it was heated at 100° with dilute sulfuric acid (containing 1% or more), the product was a viscid oil, boiling above 100°, seemingly the product of condensation of a hydrocarbon (diisopropenyl) formed by the action of very dilute acids.

"After heating for 20 to 30 minutes in a water bath with hydrochloric acid of 0.1% a very mobile, liquid hydrocarbon, boiling at 68° to 69°, was obtained. The hydrocarbon is C<sub>6</sub>H<sub>10</sub>, diisopropenyl."

In 1892, F. Couturier<sup>2</sup> writes: "β-dipropylene polymerises with extreme ease, which does not take place with the isomeric compounds having the normal chain, such as diallyl. This property renders all of the reactions with this hydrocarbon very difficult. The polymerization is produced by heat alone, and the liquid is transformed into a viscous product, which cannot be distilled. Calcium chloride acts in the same manner in the cold, when it is allowed to stand in contact with the hydrocarbon for a long time."

"I have tried to hydrate β-dipropylene by means of sulfuric acid. But this attempt was rendered fruitless by the extreme ease with which this hydrocarbon polymerises. When the hydrocarbon is added to sulfuric acid, cooled to zero, the liquid becomes colored and viscous. When the product is cooled with ice, there separates a resinous material, which agglomerates and which yields no volatile products when distilled with steam. This resinous product is soluble in ether, chloroform, acetic acid, and benzene; but none of these solvents gave a product suitable for analysis."

Referring to the above article, Perkin, Jr. says: "In 1892, Couturier added another member to the rubber series, since he found that diisopropenyl (dipropylene) polymerises very readily, *e. g.*, by the action of heat." Perkin, Jr. adds that the agglomeration and the solubilities of Couturier's "resin" are "properties somewhat resembling those of freshly precipitated rubber."

The fact nevertheless remains that Couturier does not intimate that his resinous product is even remotely related to rubber, and personally I do not see how *his* work added "another member to the rubber series."

In 1900, Kondakow<sup>3</sup> investigated the behavior of diisopropenyl towards alcoholic potash, in order to determine whether this hydrocarbon is polymerized under these conditions. He says: "When this hydrocarbon is heated with alcoholic potash (1 part potassium hydroxide to 3 parts of alcohol) at 150° for five hours, a part of the hydrocarbon is

<sup>1</sup> *J. Chem. Soc., Abstr.* 58, 728 (1890) (from *J. Russ. Chem. Soc.*, 21, 434).

<sup>2</sup> *Ann. chim. phys.*, 26, 489, 491.

<sup>3</sup> *J. prakt. Chem.*, 62, 175, 176.

polymerised, and the remainder is unaltered. The remaining, unaltered portion of the diisopropenyl boils at  $69.5^{\circ}$  to  $70^{\circ}$ ."

"As regards the polymerisation product which is obtained by heating diisopropenyl with alcoholic potash, its properties recall those of caoutchouc or of the polymer of styrene. The product is a leather-like, elastic mass, nearly white in color, is not volatile with steam, is insoluble in water, but is soluble in hydrocarbons, ether and alcohol."

In 1901, Kondakow<sup>1</sup> published a short paper on "A Remarkable Case of Polymerization of Diisopropenyl (Dimethyl-2,3-butadiene-1,3)." He placed two lots of 20 grams each of diisopropenyl in two 50 cc. flasks, the flasks being about two-fifths full of the liquid. "The flasks were then sealed and allowed to stand in diffused daylight for about one year. At the end of this time, the liquid was found to have been converted into a white solid mass, which completely filled the flasks in the form of a sponge. On opening the flasks, neither increase or decrease in pressure was observed and no trace of the original hydrocarbon was found. Under the microscope the substance seemed to be amorphous, and it is tasteless and odorless, and elastic like rubber; it also reminds one of rubber in its behavior on chewing, and it appears to be unchanged in the air. The substance is absolutely insoluble in benzine, ligroin, ligroin chloroform, carbon disulfide, ether, alcohol, acetone and turpentine; it swells up in benzene. It is distinguished from rubber by its behavior towards these solvents."

Then Kondakow adds: "I can only point out that the second polymer is clearly or sharply distinguished from the previously described polymer (the one soluble in alcohol) by its physical properties; it appears to be a higher polymerisation-product than the first."

This spontaneous polymerisation of 2,3-dimethylbutadiene to a rubber-like substance, observed by Kondakow, is strikingly like the spontaneous polymerisation of isoprene to a rubber-like substance, observed by Tilden. There also seems to be some reason for believing that this similarity in the behavior of the two hydrocarbons, and a possible relationship of their polymerisation-products, were discussed in Kondakow's original paper<sup>2</sup> of 1901. It has been stated that this paper was written in Russian, and the Editor of the *Journal für praktische Chemie* cut out some of the theoretical speculations of Kondakow, hence, they did not get into the German or English literature. At all events, Kondakow<sup>3</sup> now claims that he, and not the chemists of Bayer & Co., was the real discoverer of the first homologous rubber. Prof. Perkin, Jr. and some others seem to support Kondakow's claim, while Prof. Harries and Bayer & Co. do not acknowledge it.

It appears to me that one of the most important arguments in favor of Kondakow's claim is found in two articles written by C. O. Weber on December 5, 1902, and January 23, 1903, for the "Gummi-Zeitung."

In his 1902 communication,<sup>4</sup> Weber says:

<sup>1</sup> *J. prakt. Chem.*, 64, 109, 110.

<sup>2</sup> See review on Kondakow's book and claims to priority, by Dr. K. Gottlöb, *Gummi-Ztg.*, 26, 1546, 1582, 1628 (1912).

<sup>3</sup> Le caoutchouc synthétique, see homologues et ses analogues, *Rev. gén. chim. pure et appliquée*, 1912, 129.

<sup>4</sup> *Gummi-Ztg.*, 1902, 207

"In the *Journal für prakt. Chemie* for 1901, Bd. 64, page 109, J. Kondakow describes a most remarkable case of the polymerisation of 2,3-dimethyl-1,3-butadiene, which substance might be more concisely termed methylisoprene.

"To those who have carefully followed the evolution of the chemistry of rubber, it is well known that Bouchardat, Tilden and I have shown that isoprene may be reconverted or polymerized into rubber. Kondakow finds that his dimethylbutadiene, a liquid boiling at  $69.5^{\circ}$ , is spontaneously polymerised, on standing for 12 months, into a white, solid, spongy, elastic mass, whose physical properties resemble those of rubber. This polymerisation-product is distinguished from rubber, however, by the fact that it is insoluble in any of the known solvents for rubber. Therefore, this product, when considered from the chemical view-point, is undoubtedly to be regarded as the first known homologue of rubber, and it affords us the first concrete example of the possibilities which are scarcely suspected at the present day, and which will find their realization with the artificial production of rubber."

"It must be apparent to every manufacturer that such a rubber (as Kondakow describes) would have an enormous importance for the industry, since this rubber, even when not vulcanized, is totally unaffected by all solvents and oils, while in the vulcanized condition it would show no tendency to swell up in liquid hydrocarbons as benzene, petroleum, etc., and in oils."

In his 1903 article,<sup>1</sup> Weber repeats his statement that Kondakow's product is to be regarded as the *first known homologue of rubber*."

In a paper written in 1912, E. Grandmougin<sup>2</sup> says: "The fact that not only isoprene, but also dimethylbutadiene may be polymerized to rubber-like substances, was recognized by Kondakow about the year 1900; and the importance of this observation, which furnished the possibility of producing homologous rubbers, was thoroughly appreciated at that time."

On the other hand, Friedr. Bayer & Co.,<sup>3</sup> of Elberfeld, in their patent of December 27, 1909, covering the method of preparing a rubber from 2,3-dimethylbutadiene, call attention to this work of Kondakow, and point out that his first product was soluble in alcohol while natural rubber is completely insoluble in alcohol; hence they conclude that Kondakow's first product was not an analogue or homologue of rubber, but was a lower polymerisation-product of the hydrocarbon. They also argue that the very insoluble second product of Kondakow is likewise no analogue of rubber, as indicated by its properties, but that it is probably a much higher polymerisation-product than natural rubber. They advise that in the process of making true 2,3-dimethylbutadiene rubber, the process must be carefully controlled by suitable tests so that the operation shall be continued until the resulting product reaches the condition of being insoluble in alcohol, but soluble in benzene.

It is also interesting to note that in "The India Rubber Journal" for February 8, 1913, page 10, is an article on the "Manufacture and Production of a Caoutchouc-like Substance." This article states:

<sup>1</sup> *Gummi-Ztg.*, 1903, 374.

<sup>2</sup> *Ibid.*, 1912, 862.

<sup>3</sup> Deutsche Patentanmeldung, F.29010, Kl. 39b, Gr. 1, vom 27 Dezember, 1909.

"The foreign correspondents of the patentee have found that the product obtained by Kondakow from  $\beta,\gamma$ -dimethylerythrene ( $\beta,\gamma$ -dimethylbutadiene) (*J. prakt. Chem.*, 64, 109-110) can be converted by heating, preferably under pressure, into a technically valuable elastic caoutchouc-like product. For example, the Kondakow product is heated for eight hours in a closed iron vessel to from  $150^{\circ}$  to  $200^{\circ}$ . A compact, elastic mass is thus obtained. Patent No. 13,591."

Regarding this insoluble product obtained by Kondakow in 1901, Prof. Harries says:<sup>1</sup>

"I know this product very intimately, since I have had it in large quantities at my disposal. It does, in fact, have a certain connection with normal dimethylbutadiene rubber, but is in itself scarcely to be looked upon as rubber, for, after it stands in the air for a short time it changes into a peculiar, sticky, tough mass, readily soluble in the usual solvents, which is certainly useless for any technical purposes. Dimethylbutadiene rubber, obtained by heating dimethylbutadiene for a long time in a sealed tube at  $90^{\circ}$ - $110^{\circ}$ , acts entirely differently."

Again, Harries says:<sup>1</sup> "On splitting up normal dimethylbutadiene rubber, a practically quantitative yield of acetonylacetone is obtained, while Kondakow's insoluble, spontaneously polymerized product, and the soluble resin formed by allowing the latter to stand in the air, both yield at the most only 40 to 50% of acetonylacetone; it is also to be noted that the two latter products also yield an unknown aldehyde, boiling at about the same temperature as acetonylacetone.

"The decomposition curves of the diozonide of normal butadiene rubber, and the corresponding curves for the diozonides of the Kondakow products show great differences."

In reply to Prof. Harries' criticism of his support of Kondakow's claim to priority, E. Grandmougin<sup>2</sup> says:

"Although the investigations of Harries and of Bayer & Co. have shown that Kondakow's product is not a true rubber, but only yields a technically useful product through polymerization by heat, this does not change my views in the matter. The fact is, that as early as the year 1902 the possibility of preparing synthetic rubber from isoprene, and homologous rubbers from the butadienes was recognized, and the importance of this observation was at that time no secret to the specialists in this field. The technical development of the discovery, especially the manufacture of the raw materials in sufficient quantity, as well as the study of the polymerization processes, belong to the following period. Later investigators, as Harries, Hofmann, Coutelle, and others, deserve the credit of having shown the possibility of the technical accomplishment of the synthesis of rubber and analogous products."

However, until some better proof is offered, I believe we shall have to regard Kondakow's products as *not* being true dimethylbutadiene rubbers.

Prof. Perkin, Jr. cites the following references as observations made by various workers "on a variety of compounds, all of which are characterized by containing the conjugated double linking,



<sup>1</sup> *Ann.*, 395, 215.

<sup>2</sup> *Chemiker-Ztg.*, 1913, 502.



"The polymerides obtained were mostly incompletely investigated, but their behaviour with solvents showed a general resemblance to that of rubber."

(1) The work of Harries<sup>1</sup> in 1901 on dihydrotoluene. Harries says: "The hydrocarbon (dihydrotoluene) resinifies readily, and on every distillation it leaves a small amount of a thick, yellow oil."

(2) The work of Klages in 1902 and 1904 on phenylbutadiene. In 1902, Klages<sup>2</sup> stated: "Phenylbutadiene boils at 94–96° under 18 mm. pressure; on distillation under ordinary pressure, it polymerizes to high boiling products. When exposed to the air, it resinifies forming a colorless balsam." In 1904, Klages<sup>3</sup> stated: "Phenylbutadiene is soluble in any proportion in ether, alcohol, and benzene, forming clear solutions; but it often changes after a few days and then gives opalescent solutions, which, after long standing, throw out white flakes. It gradually polymerises to a thick mass, which is insoluble in alcohol and ether, but is soluble in benzene."

(3) The work of Kronstein<sup>4</sup> in 1902 on cyclopentadiene. Kronstein gives the following: "The formation of dicyclopentadiene (from cyclopentadiene) requires several days at certain temperatures. It was to be expected that the formation of the dicyclopentadiene could be hastened by heating. For this purpose, I heated pure cyclopentadiene in a closed tube at 160°. After heating for five hours, the liquid commenced to become cloudy, and a white, solid substance separated in the form of a white powder. The separation of this solid continued as long as there was any unchanged cyclopentadiene present. The end-product is a slightly yellowish colored, opaque, solid substance."

"This solid substance may be completely reconverted into the monomolecular cyclopentadiene by the action of heat. The new polycyclopentadiene is insoluble in all solvents."

(4) The work of Willstätter and Veraguth<sup>5</sup> in 1905 on  $\alpha$ -cyclooctadiene. These investigators state the following: "Cyclooctadiene may be purified by distillation over metallic sodium in vacuum; under 16.5 mm. pressure, it distills over as a clear, limpid oil and leaves little solid residue. It cannot be distilled under ordinary pressure, for as soon as it commences to boil the thermometer rises to 135–150°, and polymerization takes place very quickly and explosively with the formation of a gelatinous mass." " $\alpha$ -Cyclooctadiene shows an unusually strong tendency to polymerise. Even after standing for a short time, the liquid is converted into a solution of the dimolecular compound, which crystallizes out on strong cooling, but again dissolves at the room temperature. On standing for two to three days at the room temperature, the hydrocarbon is converted into a hard mass, which consists for the most part of the crystalline dicyclooctadiene; on the other hand, rapid polymerization at elevated temperatures converts about half of the hydrocarbon (1.8 grams out of 4 grams) into a higher molecular polymerisation-product."

"The dicyclooctadiene is very readily soluble in all organic solvents

<sup>1</sup> *Ber.*, 34, 303.

<sup>2</sup> *Ibid.*, 35, 2650.

<sup>3</sup> *Ibid.*, 37, 2310.

<sup>4</sup> *Ibid.*, 35, 4151.

<sup>5</sup> *Ibid.*, 38, 1976, 1977, 1979, 1980, 1981.

even in the cold. On standing in the air, it rapidly resinifies with absorption of oxygen."

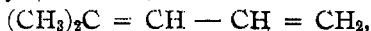
"The higher molecular polymeride, formed at elevated temperature, forms a powder which does not melt up to 300°, and is extremely insoluble, crystallizing only from xylene. It remains unaltered in the air. It was not obtained pure enough to give good results on analysis, but it was shown to contain considerably more oxygen than dicyclooctadiene."

"This tendency towards polymerization exhibited by  $\alpha$ -cyclooctadiene is of especial interest, owing to the recent important investigations of C. Harries, according to which there is indicated a connection between rubber and cyclooctadiene, and a cyclooctadiene appears to be the actual parent substance of para-rubber."

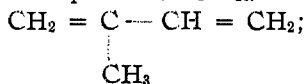
In 1907, Willstätter and Veraguth<sup>1</sup> described an isomeric cyclooctadiene, which they distinguished from the above described compound ( $\alpha$ -cyclooctadiene) by the term  $\beta$ -cyclooctadiene. They stated: "The chief distinction between the two cyclooctadienes consists in the stability of the  $\beta$ -hydrocarbon; while  $\alpha$ -cyclooctadiene polymerizes rapidly and often with an explosion, the  $\beta$ -compound suffers no change either by keeping for several months or by continued boiling."

(5) The work of Willstätter and Bruce,<sup>2</sup> in 1907, on bromobutadiene. They state: "Bromobutadiene is a readily mobile, very volatile liquid. On keeping, it is changed into a dark brown thick mass having little solubility; it is apparently a polymerisation-product."

The work of E. Knoevenagel,<sup>3</sup> in 1906, on 1,1-dimethylbutadiene should also be mentioned. He says: "When isoheptadienic acid is treated with dilute sulfuric acid, carbon dioxide is split off, and there results, possibly with the intermediate formation of a lactone—as the chief products, two hydrocarbons,  $C_6H_{10}$ ,



and a dimolecular substance,  $C_{12}H_{20}$ ; this dimolecular compound is probably formed by the polymerization of the hydrocarbon,  $C_6H_{10}$ , in a manner similar to the formation of dipentene,  $C_{10}H_{16}$ , from isoprene,  $C_5H_8$ ,



accordingly, it would have to be regarded, like dipentene, as a cyclohexene derivative. Together with the two above mentioned hydrocarbons, a small amount of a higher boiling product was obtained, which, according to its boiling point, may be regarded as a trimolecular hydrocarbon,  $C_{18}H_{30}$ .

"The detailed description of the properties of these substances, and their relation to already known compounds will be given later in another place. Moreover, in view of the formula suggested by Harries for para-rubber, it is proposed to trace the possible connection which perhaps exists between the above mentioned hydrocarbons—more especially those having a straight chain of carbon atoms—and the rubber group; the connection may possibly be found in a different manner of polymerization."

<sup>1</sup> Ber., 40, 957, 964.

<sup>2</sup> Ibid., 40, 3994.

<sup>3</sup> Z. angew. Chem., [2] 19, 1330.

A careful review of the literature shows, therefore, that with the exception of Kondakow's leather-like, alcohol-soluble product and his higher molecular, insoluble polymeride obtained from 2,3-dimethylbutadiene, none of the earlier investigators described a rubber-like polymeride, or even anything approaching rubber-like, as resulting by the polymerization of an isomer or homologue of isoprene.

By some stretch of the imagination, we might possibly regard some of the solubilities of certain of these polymerides as resembling the solubilities of rubber, yet in all other important respects they were totally unlike rubber, *and by no means could they be termed isomeric or homologous rubbers.*

Prof. Perkin, Jr., sums up the position of synthetic rubber at the beginning of the year 1909 with these words:

"It was generally recognized that most compounds containing the conjugated double linking showed a tendency to polymerise, in some cases very readily, but in others with difficulty. The polymerides varied from sticky, indefinite substances, through well defined rubbers, to hard resins; their properties also varied somewhat with the method of polymerisation and with the molecular weight of the hydrocarbon polymerised. The methods of polymerisation included spontaneous polymerisation and polymerisation due to heat, sunlight, or the action of various chemical reagents, such as acids and alkalies. But, in most of these cases the methods in use were uncertain, wasteful or slow."

With one very important modification, I think we can all agree with this statement of Prof. Perkin, Jr. The part of his summary which I feel is *very* misleading, is his statement that "the polymerides varied from sticky, indefinite substances, *through well defined rubbers*, to hard resins." For, *with the exception of the work of Bouchardat, Tilden, Weber, and Wallach, on isoprene, and that of Kondakow on dimethylbutadiene*, there is, to the best of my knowledge, no reference in the literature by any investigator where "a well defined rubber" was ever formed as a polymeride from any conjugated double linkage compound, prior to the work of Prof. Harries and of Bayer & Co. in the year 1909.

HOBOKEN, N. J.

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## NEW BOOKS.

**Les Progrès de la Chimie en 1912.** Traduction Française autorisée des "Annual Reports on the Progress of Chemistry for 1912, Vol. IX," issued by the Chemical Society, London, Traducteurs, D. FLORENTIN, E. GELIN, P. HUCHET, M. DRECO, J. SAPHORES, P. POURQUERVY. Paris: Librairie Scientifique A. Hermann et Fils. 1913. Price, 7,50 francs.

These well-known "Annual Reports" for 1912 contain the following divisions: General and physical chemistry, by G. Senter; inorganic chemistry, by E. C. C. Baly; organic chemistry, I, aliphatic series, by H. R. LeSueur, II, homocyclic series, by K. J. P. Orton, III, heterocyclic series and stereochemistry, by A. W. Stewart; analytical chemistry, by G. Cecil Jones; physiological chemistry, by W. D. Halliburton; agricultural chemistry and vegetable physiology, by A. D. Hall; mineralogical chemistry, by Arthur Hutchinson, and radioactivity, by Frederick Soddy.