



The World's Largest Open Access Agricultural & Applied Economics Digital Library

This document is discoverable and free to researchers across the globe due to the work of AgEcon Search.

Help ensure our sustainability.

Give to AgEcon Search

AgEcon Search

<http://ageconsearch.umn.edu>

aesearch@umn.edu

*Papers downloaded from **AgEcon Search** may be used for non-commercial purposes and personal study only. No other use, including posting to another Internet site, is permitted without permission from the copyright owner (not AgEcon Search), or as allowed under the provisions of Fair Use, U.S. Copyright Act, Title 17 U.S.C.*

No endorsement of AgEcon Search or its fundraising activities by the author(s) of the following work or their employer(s) is intended or implied.

TE 141 (1929)

USDA TECHNICAL BULLETINS

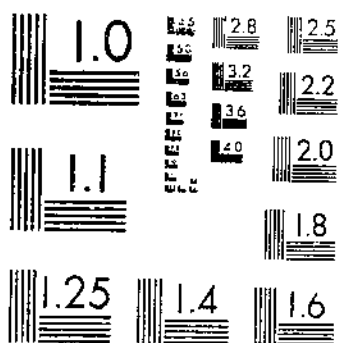
UPDATA

THE SPONTANEOUS COMBUSTION OF HAY

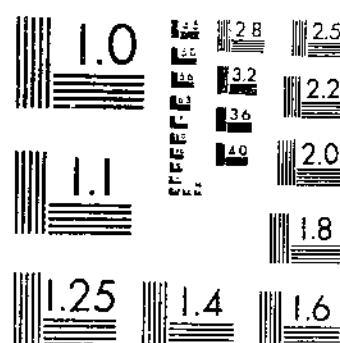
BROWNE, C. A.

1 OF 1

START



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

THE SPONTANEOUS COMBUSTION OF HAY

By CHARLES A. BROWNE

Chief, Chemical and Technological Research, Bureau of Chemistry and Soils

CONTENTS

	Page		Page
Introduction.....	1	New suggestions as to the cause of the spontaneous combustion of hay—Continued.	
Review of previous theories.....	3	Oxidizable, unstable, fermentation products as a cause of spontaneous heating.....	25
Ancient observations.....	3	Experimental production of unstable, unsaturated compounds from sugar.....	26
Ancient theories of friction and occluded heat.....	3	Rate of oxidation in fermenting hay.....	28
Theories of vital heat.....	5	Variations of moisture content in fermenting hay.....	28
Chemical theories.....	7	Spontaneous ignition of horse manure at Arlington, Va.....	29
Pyrophoric carbon theory of Ranke.....	8	Production of compounds of high carbon content at low temperatures.....	32
Low-temperature carbonization theory of Miele.....	10	Temperature of the exothermic reaction of hay.....	33
Experiments of Haldane and Makgill.....	13	Length of time necessary for the spontaneous ignition of hay.....	33
Enzymic-reduction theory of Tschirch.....	14	Unsaturated substances occurring naturally in hay.....	35
Burr's theory of heat-resisting enzymes.....	16	Need of future investigations.....	36
Hildebrandt's criticisms of the enzymic theories.....	17	Literature cited.....	37
The catalytic oxidation theory of Rookhout and De Vries.....	18		
Lauppper's theory of pyrophoric iron.....	19		
Divergence of opinions.....	23		
New suggestions as to the cause of the spontaneous combustion of hay.....	23		
Factors in the spontaneous ignition of oil-treated cotton.....	23		

INTRODUCTION

One of the oldest observations with reference to the storage of agricultural products is that certain materials, such as hay, cattle feeds, horse manure, and many forms of cellular wastes, undergo a process of heating, the rise of temperature under some conditions advancing to the point where spontaneous ignition is produced. The economic losses from fires that develop from this cause amount each year in the United States to many millions of dollars.¹ (Fig. 1.) Unfortunately, the data for making an accurate estimate of these losses are very meager. The statistics of American fire losses, compiled annually by the National Board of Fire Underwriters, give for the reported destruction of property from spontaneous combustion in the United States during the year 1925 a loss of \$17,391,393; dur-

¹ One of the earliest references in the United States to the importance of spontaneous combustion was made by Henry Wallace (29, p. 85-90).²

² Italic numbers in parentheses refer to "Literature cited," p. 37.

ing 1926, \$15,498,812; and during 1927, \$13,640,804. In order to cover the losses not reported to its actuarial bureau the National Board of Fire Underwriters adds an additional 25 per cent to its compilations, which would bring the estimated total loss from spontaneous combustion in the United States to \$21,739,241 for 1925, to \$19,373,515 for 1926, and to \$17,051,005 for 1927. The actual annual losses from spontaneous combustion in the United States are, however, much greater than the amounts just mentioned, for the reported destruction of property from unknown causes of fire, of which spontaneous combustion undoubtedly formed a high percentage, was \$199,179,533 in 1925, \$202,369,737 in 1926, and \$171,038,429 in 1927. A rough estimate of the chemical engineering division of the Bureau of Chemistry and Soils, based upon the reports of farm mutual insurance associations in various States and of other organizations, indicates that in farm fires alone the loss from spontaneous combustion in the United States may exceed \$30,000,000 a year, which is 20 per cent of the total estimated annual loss of \$150,000,000 from fires on farms and in rural communities.

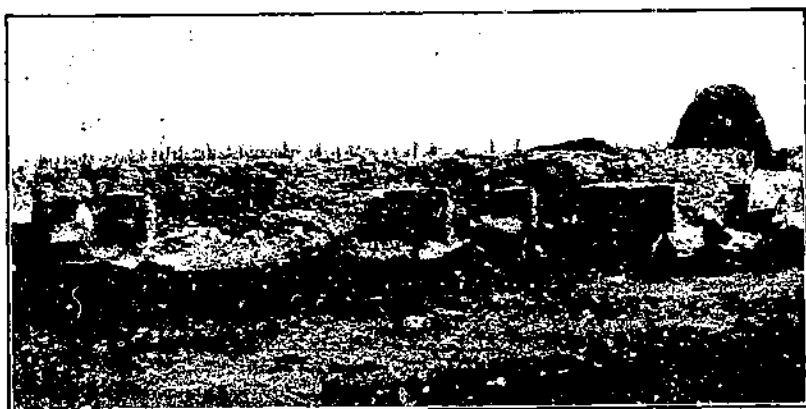


FIGURE 1.—All that was left of a Maryland barn destroyed by the spontaneous ignition of the hay in it

Statistics of other countries indicate an equally high percentage of losses from spontaneous combustion. The fire marshal's office of Toronto, Canada, estimates that in 1920 the Province of Ontario alone suffered a loss of nearly three-quarters of a million dollars from the spontaneous combustion of hay and other farm produce. G. Lauppper estimates that at least 0.5 per cent of the hay supply of Switzerland is lost each year from spontaneous combustion, the total annual destruction of farm produce and buildings from this cause amounting for this small country to 18,000,000 francs or \$3,600,000. Estimates of the losses in other countries are not available, but the proportional destruction of property elsewhere from spontaneous combustion must have been equally high. To these losses from fire must be added the losses in the value of produce from overheating (which in many cases proceeds to the point of carbonization without final ignition), that do not appear in the statistical estimates of fire losses. What this secondary loss may amount to can be inferred from the statement of Lauppper that for every 25 actual fires result-

ing from spontaneous combustion in Switzerland there were not less than 167 cases of carbonization, as a result of overheating. The great possibility of fires from spontaneous combustion is apparent from the fact that the accident of exclusion of sufficient air is all that prevents a carbonization from developing into an ignition.

REVIEW OF PREVIOUS THEORIES

ANCIENT OBSERVATIONS

For the oldest observations upon spontaneous combustion we must go back to antiquity. The storing of cut grass for the sustenance of sheep, goats, horses, and other domesticated animals during the winter was practiced by man at a very early date, and the phenomenon that green grass when piled in heaps undergoes spontaneous heating with danger of final ignition was undoubtedly noticed long before the rules of agricultural procedure were reduced to writing. A proper method of curing the cut grass intended for the winter feeding of cattle was gradually evolved as a consequence of long experience, with the result that in the ancient classical works upon agriculture are definite practical rules for preventing the spontaneous heating and combustion of hay. Columella (8), a Roman writer of the first century A. D., makes the following statement, for example, in his classical treatise upon agriculture:

The best time to cut hay is before it dries up: first because it gives a larger yield and second because it furnishes a product that is relished better by animals. There must, however, be a certain mean observed in curing hay in order that it may not be gathered either too dry or too green. In the former case, if it has lost all its juice, it is only good for bedding; in the latter case, if it retains too much of its juice, it rots on the scaffold and when it has become hot often ignites and catches fire.

The elder Pliny (23), a contemporary of Columella, lays down the following rule in his famous encyclopaedic *Natural History*:

... When the grass is cut it should be turned towards the sun and must never be stacked until it is quite dry. If this last precaution is not carefully taken, a kind of vapor will be seen arising from the rick in the morning, and as soon as the sun is up it will ignite to a certainty and so be consumed.

In this passage Pliny seems to indicate that solar heat is the final cause of ignition.

ANCIENT THEORIES OF FRICTION AND OCCLUDED HEAT

The ancient Greeks, who were keen speculators in every field of knowledge, naturally developed a theory for spontaneous combustion. At a very early period of their civilization they were familiar with the process of producing fire by the friction of wood, a method employed by nearly all primitive races, and at a later date, when they began to philosophize, the Greeks made this idea of friction the basis of their explanation of spontaneous combustion. Many illustrations of this could be given, one of the best known being a comment that the Greek historian Thucydides (26) makes in his famous *History of the Peloponnesian War*, where, in describing a conflagration of wood, pitch, and sulphur which was set by the Peloponnesians during the siege of Plataea, he remarks:

The consequence was a fire greater than any one had ever yet produced by human agency, though it could not of course be compared to the spontaneous conflagration sometimes known to occur through the wind rubbing the branches of a mountain forest together.

The explanation of the action of friction in setting fire to wood or other substances, according to the Greeks, was a loosening and coalescing of the minute scattered particles of fire which they supposed to exist in every combustible material. This old concept of flammable substances containing a hidden heat that was ready to break into fire under favorable conditions was inherited from the Greeks by the philosophers of the later Roman and medieval periods and has persisted even until comparatively modern times. Bacon (*1, v. 1, p. 186-187*), the Elizabethan philosopher, in his famous *Novum Organum*, made this idea the basis of his explanation of spontaneous combustion:

All herbs and green and moist vegetables seem to contain some secret heat, though so small as to be imperceptible to the touch in small portions; but when many are joined, and close shut up together, so that their spirit cannot breathe out into the air, but the parts must mutually foment and cherish each other, a manifest heat is produced, and sometimes a flame if the matter is disposed thereto.

The doctrine of hidden particles of fire was especially elaborated by the Greek philosophers of the atomic school, Democritus, Epicurus, and their followers. Their ideas were made use of by the Latin poet Lucretius (*19, v. 1, p. 40*) in his scientific poem upon *The Nature of Things*. In commenting upon the spontaneous origin of forest fires, as previously given by Thucydides, Lucretius makes the following argument:

But it often comes to pass on high mountains, you say, that contiguous tops of tall trees rub together, the strong south winds constraining them to do so, until the flower of flame has broken out and they have burst into a blaze. Quite true and yet fire is not innate in the woods; but there are many seeds of heat, and when they by rubbing have streamed together, they produce conflagrations in the forests. But if the flame was stored up ready made in the forests, the fire could not be concealed for any length of time, but would destroy forests, burn up trees indiscriminately.

Although this idea of forest conflagrations being produced by the continual rubbing together of the branches of trees in the wind rests upon a mistaken assumption, the old Greek theory of the spontaneous production of fires by friction found a very general acceptance until comparatively modern times. Without giving an account of the development of this theory in all its historic details it might be mentioned that the Arab writer Ben Mohalhal about 942 A. D. referred to the fact that the leaves of a cane which grew in Kabul were ignited by the rubbing of the leaves against each other in the wind, and that as late as 1644 the celebrated French philosopher Descartes (*9*) in his *Principia Philosophiæ* explained the spontaneous heating of vegetable tissues upon the basis of an inner friction produced by the movement of plant juices through the dry contracted cellular vessels.

The ancient conception of hidden or included fire was also held by the famous Dutch chemist Boerhaave (*4, pt. 3, p. 175-176*) of the University of Leyden, who in his *New Method of Chemistry* describes the first attempt to analyze the products that were formed during the spontaneous heating of hay.

1. Throw together any of the tender, green and succulent parts of recent vegetables, whether acid or alkaline, in a large heap, in the warm open air, and press them down with an additional weight, if their own be inconsiderable; and the middle part of the heap will, in a little time, spontaneously conceive a small degree of heat, and pass successively thro' the other degrees, till it comes to a state of ebullition. In the space of three days, from the first putting them together, they will yield a heat, perceivable by the hand, equal to that of the human body in a state of health; by the fifth it will be too great for the hand to bear without pain; and lastly, by the sixth, seventh, or eighth day, the juices will generally appear ready to boil, and sometimes the matter will even flame and burn away. (2.) By this spontaneous operation, the vegetable acquires an abominably putrid, stercoraceous, or cadaverous, taste and odour; and turns entirely into one soft, similar, pappy mass, or *crassamentum*, greatly resembling fetid human excrement in scent, and putrefied flesh in taste. (3.) If now this fetid matter, thus obtain'd, be directly, whilst it remains in its fetid state, committed to a glass retort, and distill'd with proper degrees of fire, there will come over, 1st, A water impregnated with an urinous spirit, perfectly like that obtainable from animal subjects, and separable by a fresh distillation, slowly made in a tall glass, into elementary water, and a large quantity of pure, white, volatile, dry alkaline salt, not to be distinguished from animal salts. 2dly, A volatile, alkaline, oily salt, that shoots in gleebs. 3dly, An exceedingly volatile and a thick fetid oil, both which are also entirely like those of animals. 4thly and lastly, the remainder being calcin'd in an open fire, affords not the least particle of fix'd salt; just as if the subject had really been of the animal, and not of the vegetable kingdom.

2. This process is truly universal, and holds equally in all kinds of vegetables, tho ever so different in their nature and virtue. I have my self made the experiment in the coldest and most succulent or watry plants, such as purslain, sorrel, etc., as well as with the hottest or most acrimonious, such as the sparges, etc., and always found it succeed; but the sooner, as the vegetables employ'd contain'd the greater quantity of oil; tho with the same phenomena. It will likewise succeed with dry vegetables; provided they be moisten'd with water before they are thrown into heaps. And thus we sometimes see that stacks of hay will spontaneously take fire and blaze away; especially if it was not well dried in the making. . .

3. . . . We see also that vegetable putrefaction is begun and promoted with heat, and finished with coction, which requires a degree of heat much greater than that excited by fermentation, as being capable of causing an ebullition in the plant, and even of turning it into flame: and indeed the immediate cause of fermentation, is the motion of the air intercepted between the fluid and viscous parts of the fermenting liquor; but the cause of putrefaction is fire it self, collected or included within the putrefying subject.

Boerhaave thus regarded the heating of hay not as a fermentation but as a putrefaction of which a collected or included fire was supposed to be the cause. Boerhaave's statement that he obtained a volatile alkaline spirit and salt (ammonia and ammonium carbonate) in the distillation of hay that had undergone spontaneous heating is one of the first references to an observation that was frequently made by later students of the subject.

THEORIES OF VITAL HEAT

Another explanation of the spontaneous combustion of hay and other plant products, which is more modern than the purely physical theory of friction, is the accumulation of vital heat. One of the oldest observed characteristics of living matter is the generation of warmth, which was noted by early man not only in the case of animals but in that of many vegetable materials, such as heaps of sprouting grain. It was supposed by many who speculated upon the subject (and the error still persists) that if the warmth generated by the tissues of living plants, such as freshly cut grass, could be completely

confined within a well-insulated space, such as the interior of a haystack, the continued accumulation of vital heat would finally raise the temperature of the mass to the point of ignition. A little reflection and experimenting are sufficient, however, to demonstrate the falsity of this theory. One need only suppose a large bathing pool, with water, atmosphere, and building at exactly blood heat, filled with men. No matter how closely crowded the bathers may be, although each is a producer of heat, the temperature of the water and of the bathroom as a whole will not rise above that of the men's bodies. The temperature of a mass of living organisms, as of bees or bacteria, is the same as that of its individual units and no more.

The production of heat by living plant cells has, however, an important bearing upon the problem of spontaneous combustion, especially in the early stages of the process. When it was recognized by physiologists that plants not only assimilate carbon dioxide and give off oxygen, but also breathe the same as animals, by taking in oxygen and giving out carbon dioxide, the generation of heat by vegetable tissues and organs began to be explained, as in the case of animals, as a result of a respiration process. The botanist Göppert (10) began in 1830 to make the first scientific experiments upon the heat developed by the respiration of plants. He showed that when grain was allowed to sprout in a wooden box, temperatures as high as 50° C. might be obtained, and he concluded from his numerous experiments that plants liberate measurable quantities of heat at all stages of growth from germination to flowering.

Göppert failed, however, to differentiate between the heat that was evolved by the respiration of the living plant and that produced by the vital processes of adhering microorganisms, a distinction that remained for Cohn (7), a plant physiologist of Breslau, to demonstrate in 1890. Cohn, by making improvements upon a device of the Würzburg botanist Sachs, constructed an apparatus by which the gas exchange of oxygen and carbon dioxide in the sprouting grain could be measured, while, so far as possible, any loss of heat by radiation and evaporation was prevented. After the compartment of this apparatus was filled with germinating malt, which had been well moistened, there developed in the first hours a rapid increase in temperature, which gradually diminished with an apparent tendency to terminate at 40° C. or at about the death point of the young plantlets. This pause in temperature increase was only temporary, however, and there soon began another rapid rise in the thermometer which finally became stationary at about 65°. The first period of heat development in this experiment, up to 40°, was explained by Cohn as resulting from the respiration of living plant cells, and the second period of heat development, up to 65°, after the life of the plant cells had been destroyed, as resulting from the vital processes of thermogenic or thermophilic microorganisms, of which, in the heating of malt sprouts, the *Aspergillus fumigatus* seemed to be the most active. Cohn demonstrated that the presence of oxygen was necessary for these biological processes of heat production by showing that when air was excluded from the vessel containing the germinated malt, the temperature came to a standstill.

In further confirmation of his demonstration of the two stages of heat production in the storage of malt, Cohn showed that if the

microorganisms adhering to the surface of the barley were destroyed by immersion of the grains in copper sulphate solution only the first stage of heat development during the sprouting of the malt took place, and the temperature did not exceed 40°C . If, however, the sterilized malt was again inoculated with the necessary thermophilic organisms the second stage of heat production could be produced, and the temperature then rose to a maximum of over 55° .

CHEMICAL THEORIES

The maximum temperatures observed in the most carefully controlled experiments upon the heating of plant materials by biological agencies rarely exceed 70°C ., which is about the thermal death point of most vegetating microorganisms. This temperature is far below the 280° or more which is supposed to be necessary for the ignition of hay, and students of the subject, therefore, felt themselves obliged to seek some other cause, either physical or chemical, which would explain the rapid rise in temperature of haystacks from the 70° to 80° which is the limit of biological heat production, to the 280° or more which is necessary for ignition.

The attention of scientists was first attracted to possibilities of a chemical nature in producing spontaneous combustion by an experiment that was performed in 1823 by the German chemist Döbereiner, who showed that when finely divided platinum is brought into contact with hydrogen gas, the hydrogen ignites. The phenomenon depends upon the fact that platinum sponge, or platinum black, has the property of condensing within its pores many hundred times its volume of the gases to which it may be exposed. The simultaneous occlusion in large volumes of oxygen from the air and of a combustible gas, such as hydrogen, in the pores of the metal brings the two into such intimate contact that they unite chemically, with ignition. In the same way carbon monoxide, ethylene, alcohol vapors, and other condensible gases can be made to ignite spontaneously.

Of a somewhat different character from the ignitions produced by the reaction between oxygen and combustible gases in the pores of intensely absorbent materials are the spontaneous combustions of substances in the so-called pyrophoric condition, by which is meant a state of material resulting from exceedingly minute subdivision of its particles that permits of such rapid atmospheric oxidation as to raise the temperature to the point of incandescence. A large number of such pyrophoric substances are known to the chemist. If lead tartrate, for example, be heated in a glass tube and air excluded the lead is reduced to the metallic condition and left in such an exceedingly fine state of division that if the tube be tightly sealed, cooled, and then reopened, the minute particles of metal upon coming in contact with the air will combine with atmospheric oxygen with such avidity as to take fire spontaneously. In a similar way, when potassium or sodium sulphates are thoroughly mixed with lampblack and ignited in a covered crucible, the salts of these alkali metals are reduced to the corresponding sulphides, which are mixed with the charcoal in such a finely divided state that the material ignites spontaneously on exposure to the air. Another mixture of similar pyrophoric character is obtained by igniting potassium or sodium alum

with lampblack, starch, or flour. Various metallic oxides, such as those of iron, cobalt, and nickel, when heated in hydrogen at low redness, especially in admixture with alumina, magnesia, or other infusible materials, are reduced and leave the corresponding metal in a very finely divided pyrophoric condition.

The employment of the principles of gas absorption and pyrophoresis as an explanation for the spontaneous combustion of hay was first made in 1872 by Buckner (24, p. 361), professor of chemistry at the University of Munich, in the following words:

If a spontaneous decomposition of hay with a consequent considerable evolution of warmth is accepted as a well established fact, it can then also be supposed, when the greatest part of the water contained in the hay has evaporated, that, as a result of the continual absorption and decomposing action of oxygen, the heat under especially favorable conditions may be raised to the point of ignition. This idea is based upon the supposition that during the progressive decomposition above mentioned the hay undergoes a kind of carbonization and that the carbonaceous residue formed in this way, similar to many other forms of carbon such as many peat carbons, mixtures of peat ash and carbon, or various mineral coals that are contaminated with finely divided pyrites may, in consequence of its great porosity and the presence of foreign substances that are susceptible to rapid absorption of oxygen and oxidation, acquire the property of a pyrophor and in the presence of a sufficient amount of air, condense the latter upon its surface to such an extent that the material becomes red hot and ignites.

PYROPHORIC CARBON THEORY OF RANKE

This conjecture of Buckner was immediately subjected to a critical test both by an actual observation of a case of spontaneous combustion and also by practical laboratory experiments by Ranke (24). His article upon the subject in Liebig's *Annalen* for 1873 is of such fundamental importance that it has been made the starting point of practically all subsequent discussions upon the subject. The reports of cases of spontaneous combustion previous to Ranke's investigations are so contradictory that many of the statements appear wholly unreliable. Ranke was one of the first persons with scientific training to describe an actual case of the spontaneous combustion of hay, and as his description enumerates practically all the details of such an occurrence and agrees so completely with later observations it has been translated as one of the best typical accounts of the phenomenon.

On my estate Lanfzorn, which is situated south of Munich about four hours by post near the Grünwald forest, a burning odor was observed on the morning of October 19, 1872, in the west corner of a large massively constructed barn.

In this section of the barn was stored a part of a crop of rye that had been harvested upon the estate and unloaded in two adjacent piles, one of which contained about 22½ tons and the other about 15 tons.

This rye had all been harvested in apparently well dried condition during excellent weather between the 5th and 10th of August. During the whole of September there was noticeable only the customary strongly aromatic odor of hay which increased in intensity until finally on the 17th and 18th of October a perceptible burnt odor began to be noticed. This empyreumatic burnt odor had become so strong on Saturday morning October 19 that my manager was convinced the interior of the mow had caught fire. He determined at once to remove the hay as carefully as possible and in case fire should be discovered to extinguish it with a large quantity of water.

All available buckets, casks and other containers were accordingly filled with water upon the scaffold of the barn above the rye and at 10:30 A. M. the removal of the hay was very carefully commenced.

It was evident that the burnt odor proceeded only from the larger of the two piles, which was bounded on the west and south by a solid wall of masonry 2 ft. thick and 17 ft. high, was open on the east side to the threshing floor

and directly connected on the north with the smaller pile of hay previously mentioned. The dimensions of the large pile were 23 ft. high, 23 ft. long and 16 ft. from front to back.

In the upper portion of the mow the rowen was sweating so strongly that drops were actually hanging on the spears of grass. The color of the entire pile so far as could be determined from the outside was a bright green and as far as the exterior was concerned no increase of temperature could be observed.

The rowen was carefully removed, principally on the side next to the threshing floor, and hauled out of the barn. On the top only the sweating portions were removed down to a depth of about 3 feet, and as the rowen at this point was in a dry and very hot state the removal of hay from the top was temporarily suspended. In continuing the removal from the side next to the threshing floor, an increase of heat began to be observed at a distance of about 1½ feet toward the center of the pile. The odor which escaped during these operations was strongly empyreumatic.

As the removal now began to be pushed more vigorously from the top there were suddenly observed at a depth of about 5 feet several sparks. At the same time smoke and flashes of sparks were suddenly observed on one of the wagons, upon which the latest removed portions of rowen were being hauled from the barn. This was about 1:30 P. M.

The entire mow and the loaded wagon were now drenched with water. The rowen that was now being hauled out was of a deep brown color and was spread out upon the grass near a pond situated behind the barn.

From now on the removal of rowen could be performed only with constant drenching with water, since almost every forkful as soon as it was taken out began to glow. It was also frequently necessary to pour water again upon the material which had been loaded since even the boards of the wagon repeatedly broke into flames. Even the rowen that had been spread out on the grass near the pond reignited repeatedly, so that it had to be extinguished three times. The material outside in the open broke out into actual flames, which was prevented inside the barn by the constant energetic drenching with water. It might be mentioned in this connection that on the following day the grass sod, upon which the removed rowen had been spread, was found to be completely burned.

On the side of the pile undergoing combustion was the above mentioned smaller pile of about 15 tons, which was found to be in perfectly good condition. In order to separate it from the other pile it was necessary to cut through a section about 3½ feet wide. In performing this work there was such a powerful out-flow of gas, probably carbon monoxide, that no workman could stay there for more than 1 to 2 minutes. The laborers became pale and livid and with a feeling of suffocation rushed out gasping for air.

Finally after it had become dark the work of removing the burning material from the barn was completed. The burnt mass formed, as it were, the core of the pile and was estimated to have a diameter of about 11 feet at the top; it extended downwards to about 1½ feet from the floor where the diameter of the hot portion, however, had narrowed down to about 4 to 5 feet. The burned area extended backwards to within about 1½ feet from the rear wall of the barn.

The condition of the burnt mass was that of an actual carbon with a retention, however, of its original structure. The form of every spear of grass and of every flower could be plainly recognized. If this grass carbon was rubbed upon paper, the latter was colored black.

Figure 2 shows the vertical section of the hay mow damaged by spontaneous combustion as described by Ranke.

Ranke attributed the repeated ignition of the carbonaceous material from the haystack to the strong absorptive power that it had for atmospheric oxygen. He next proceeded to prove this theory by means of a series of experiments, which he carried out at Munich in the laboratories of Liebig and Buckner. He found first that when the rowen was heated to such a temperature that all volatile empyreumatic substances were expelled from the residual carbon, the latter upon exposure to the air possessed no pyrophoric properties. When, however, the rowen was carbonized between 250° and 300° C. in a

flask placed on an oil bath, the resultant carbon after exposure to the air began to heat and then suddenly became red hot in a number of places. Since spontaneous ignition did not take place when the empyreumatic substances were completely removed from the carbon, Ranke concluded that these volatile products of destructive distillation very probably played some rôle in the phenomenon of self-ignition, perhaps similar to that observed in the familiar spontaneous ignition of oily waste.

Ranke states in concluding his article that the high temperature of 300°C ., which seems to be necessary for the formation of pyrophoric carbon in a haystack, is possible only by reason of the excellent insulating properties of the heavily compacted rowen. The heat which is developed in the preliminary fermentation processes and afterwards increased by the progressive chemical decomposition of the rowen is mostly retained in the interior of the stack with but little loss by radiation.

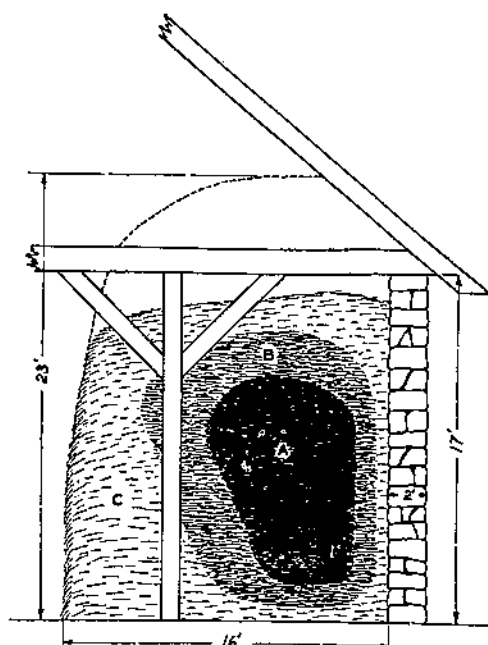


FIGURE 2.—Vertical section of hay now damaged by spontaneous combustion at estate Laufzorn, near Munich, October 19, 1872, according to description of Ranke. A, completely charred hay; B, partly charred hay; C, uninjured hay. After Medem (20)

LOW-TEMPERATURE CARBONIZATION THEORY OF MIEHE

In the subsequent development of Ranke's pyrophoric carbon theory, a number of writers, in order to avoid the difficulty of explaining high temperatures, have adopted the view that carbonization can be produced at much lower temperatures than the 250° to 300°C . which Ranke employed in his laboratory

tests. One of the chief supporters of the low-temperature carbonization theory was Miehe (21), who in 1907, while he was instructor in botany at the University of Leipzig, published a very instructive little book upon *The Spontaneous Heating of Hay*. Miehe in this work made a very exhaustive study of the thermophilic microorganisms that are concerned in the spontaneous heating of hay, chief among which is an organism discovered and named by him *Bacillus calfactor*. The general conclusions of Miehe upon the biological and chemical factors that are involved in spontaneous heating and combustion are translated from the following summary given at the close of his book (21, p. 116-121):

That heat is generally produced by plants is made apparent when they are piled together in large quantities as already indicated by Göppert. In such cases the outer layers hold the heat back so that it can not escape as fast as it is produced. The temperature must consequently increase. But with the rise of temperature, the intensity of respiration also increases, this in turn

causing more heat to be produced. As a result of this a large part of the carbohydrates (sugar, starch, etc.) is consumed, as is shown by the results of analyses in Chapter III. Finally the heat becomes so great that it kills the plants, which thus virtually breathe themselves to death. Since the thermal death point for grasses is about 45°, this will be the temperature attained by such living plants under these conditions. The increase in temperature would have to terminate here, were it not for the development of the *Bacillus calfactor*.

The above remarks apply in even greater degree to the bacteria and molds. The thermophilic bacillus germinates rapidly at 40° and multiplies very quickly, as shown in Chapter VII, as soon as it can utilize the excellent supply of nutrients that are now made available in the exuding juice of the dying plants. Its respiration energy will become correspondingly intense, so that the temperature again increases until the maximum for this bacillus is also reached, that is to say, a temperature of about 70°. The vegetative organisms now die and only the spores are left. Spontaneous heating has thus reached its highest point.

This picture of the process of spontaneous heating only applies when wilted plants, that is to say, only such as are still partly alive and breathing, are piled together in large heaps. If the plant tissues are already dead, then the microorganisms are the only agencies that accomplish the whole process."

* * * * *

During the whole course of spontaneous heating large quantities of the imbibed water contained in the hay are evaporated, so that the hay becomes gradually dry. In this way heat is naturally used up. If the mass of material, which is undergoing spontaneous heating, is very moist then the production of heat will be correspondingly slight, since it is self-evident that a large amount of warmth is taken up in raising the temperature of a great quantity of liquid. For this reason the dung piles, for example, which Holdeleiss drenched with liquid manure, remained much cooler. The apparent greater heating propensity of those dung piles that were treated with kainit and mixtures of superphosphate and gypsum depended partly upon their looser structure and partly upon the partial desiccation which resulted from the water absorption of the salts.

Finally, if upon the basis of our experience we attempt to define briefly the conditions under which spontaneous heating takes place, we would mention two points of importance, viz, first the size of the piles and second the water content of the hay.

The greater the piles are made, the quicker the maximum temperature will be reached and the longer the heat that is developed will be retained, since the larger quantity provides a greater reacting mass and at the same time a more effective insulation. It can readily be imagined that in piles of many tons the high temperature may be maintained for months in the entire inner core with the result that the carbonization process can proceed to a very wide stage. If the piles are smaller (1 or 2 tons) the maximum heat may indeed be still attained but the temperature diminishes more quickly. Finally with still smaller piles only slight elevations of temperature are reached and the cooling off process takes place even more rapidly.

The second determining factor is moisture. Its presence in sufficient quantity is absolutely necessary for the development of microorganisms. If the plants are very juicy or if the mass of material for other reasons is very moist, it will then sink together very compactly and a different kind of fermentation, resembling more putrefaction, will develop, which is probably only a consequence of the more limited supply of oxygen. Heating will also develop but, for the reasons previously indicated, will remain comparatively slight. The product will resemble manure. Molds especially develop with excessive moisture.

With an average moisture content of 36 per cent, such as is found in wilted hay, the process of spontaneous heating proceeds in the normal way. If the water content is lower, spontaneous heating will develop only incompletely, in case not very large masses of hay are employed. Completely dry hay will heat either not at all or only imperceptibly. If a normal course of spontaneous heating is desired, as in the preparation of "brown hay", the hay should have a moisture content of about 30 per cent and be piled in heaps of only medium size. Palk regards about 2 to 2½ tons as the most suitable quantity.

If the piles are very large, bad consequences develop and this leads us finally to an exceedingly important practical question, namely, that of spontaneous combustion.

What is the connection between spontaneous heating and spontaneous combustion? That both processes do not have a common origin but only exceedingly indirect relations to each other, is evident from our preceding discussions without further remarks. Microorganisms can never produce by their vital processes a higher temperature than they can endure themselves. Yet for the ignition of hay-like substances a temperature of at least 300° is necessary. How can this happen?

I would like at this point to quote in a few words a case of spontaneous combustion which was observed and described 33 years ago by H. Ranke with most satisfactory attention to details and which possesses an especial value because of the experimental evidences attached thereto (the only ones of their kind so far as I am aware).

As the account of Ranke's observations and experiments has already been quoted, Miehe's abstract need not be given. After mentioning that Ranke was unable to explain how a temperature of 300° C. could develop in the interior of a haystack, Miehe continues:

We need at this point before everything else new observations. It should be established how high the temperature can rise in a large hay stack of some 25 tons which is allowed to remain in a completely undisturbed condition. It would not be permissible to make the measurement in the usual manner of boring in a hole and inserting a thermometer. Instead of this a maximum registering thermometer or better a thermometer with self-registering distant connection should be previously packed inside. If holes are bored, the possibility is not excluded that, by the action of the copious supply of entering oxygen, the actual ignition process may start and the temperature go up. By such a measurement as this a great deal of light would be thrown upon the whole process. I regard it as highly possible that a higher temperature than 70°, or at the utmost 80°, would never be observed.

I believe that carbonization may indeed take place even at this temperature, for it must be considered that the action continues for a considerable time, even for months. The hay undergoes so to speak a dry distillation, in which the elements of the organic compounds are rearranged; new volatile compounds of simpler composition are set free and the material remaining behind approaches more and more the composition of pure carbon. That oxidations still take place above 75° and 80° has already been indicated by the experiments of Schlösing and of Boekhout and DeVries. The carbon is of an extremely fine porous structure, each cell retaining its structure. It is plausible to suppose that such carbon may condense oxygen in a manner similar to finely divided platinum (platinum sponge). It would then perhaps similar to platinum sponge acquire a strong oxidizing power and perform oxidations that would be possible normally only at a much higher temperature. It could exercise this oxidizing effect either upon itself or upon the absorbed easily oxidizable gases, such as hydrogen, phosphine, volatile hydrocarbons (methane, ethylene, etc.), that are produced by the slow distillation or decomposition of the organic constituents of the hay. Such oxidations might perhaps take place even in undisturbed piles of hay after a certain interval of time when the ingress of oxygen was limited. The temperature would then slowly increase. Or, as seems more probable, the oxidations would develop only when an abundance of oxygen can enter, or in other words when the pile is torn open or when air passages are created intentionally or unintentionally. In fact it is the general consensus of opinion (see Medem and other writers) that ignition is only produced when free entrance is given to the air by the insertion of poles, construction of air pits, opening up of the stack, etc.

An approximate picture of the process of spontaneous combustion might be constructed in the above way. Complete certainty can be realized, however, only (to repeat my former statement) when it has been definitely established how high the temperature can go in an undisturbed hay-stack of great dimensions and how long a temperature of 70° can be maintained there. In the second place it must be demonstrated experimentally whether plant materials at this temperature and within this time can be converted into a carbon-like mass, that is to say whether the same result can be accomplished at medium temperatures over a long period of reaction that is attained at higher temperatures in a short period such as in the dry distillation of wood. In the third place it must be shown that such a mass will ignite spontaneously if provision is made for the access of sufficient oxygen.

These experiments must finally be made both with and without the preliminary action of microorganisms in order to determine whether the latter provide only the heat or also the easily oxidizable compounds which in one way or another participate in the conditions that give rise to spontaneous ignition.

EXPERIMENTS OF HALDANE AND MAKGILL

Miehe's division of the biological phases of spontaneous heating into a lower-temperature period of chemical oxidation and a higher-temperature period of microorganic oxidation was confirmed in 1923 by Haldane and Makgill (11), who determined the rates of absorption of oxygen and liberation of carbon dioxide in a sample of wetted hay at different temperatures. The results of their observations are given in Table 1 (11, p. 332).

TABLE 1.—Rates of absorption of oxygen and liberation of carbon dioxide by wetted hay

Duration of experiment	Temperature	Time exposed	Oxygen absorbed per hour by 100 grams of hay	Carbon dioxide produced per hour by 100 grams of hay
Hours	°C.		C. c.	C. c.
1	35-41		19.05	14.58
1½			13.32	9.72
2¼			7.26	6.80
5½			7.02	5.81
7			9.54	9.75
8¼			14.40	18.72
9¼			33.30	35.64
10¼			45.00	67.88
22¼			263.16	295.58
23¼			277.68	315.57
24¼	51-52	20 minutes	45.90	64.42
24¾		55 minutes	25.74	37.55
25¼		1½ hours	11.28	11.28
26¼		2¼ hours	6.53	7.12
27¼		3¼ hours	8.91	14.85
28¼		4¼ hours	10.09	13.80
33¼		9¼ hours	60.19	55.40
44½		20½ hours	369.36	327.24
45		21 hours	357.04	314.28
45¼		15 minutes	347.13	299.25
46¼	60-62	1 hour	267.90	176.00
47¼		1¼ hours	189.72	177.48
48		3¼ hours	212.65	180.57
50		4¼ hours	196.02	172.85
50¼		5 minutes	67.02	65.70
50¾	70-72	20 minutes	12.85	14.07
51¼		50 minutes	12.24	10.40
52¼		2¼ hours	14.11	8.56
55		4¼ hours	8.65	6.31
59¼		8¼ hours	7.77	4.06
68¼	81	17¼ hours	5.94	4.60
71		30¼ hours	6.30	3.42
77¼		3 hours	12.75	8.42
78¼	90-91	20 minutes	18.36	15.12
78¾		35 minutes	23.04	16.92

In commenting upon these results Haldane and Makgill make the following remarks:

At first sight the extraordinary fluctuations in the rate of oxidation during this experiment might seem unintelligible; but in reality these fluctuations not only confirm the bacteriological conclusions of Miehe, but show that side by side with the bacterial oxidation there is what may be distinguished as a simple chemical oxidation. The latter oxidation diminishes with lapse of time in a manner similar to the chemical oxidation of coal at low temperatures, but is more complete, as shown by the fact that the volume of carbon dioxide liberated corresponds much more nearly to the oxygen which disappears.

It seems evident that during the first four hours the oxidation was a simple chemical one, diminishing in the usual manner as the oxidisable material became exhausted. Meanwhile, however, bacteria were developing owing to the moisture and after six hours their activity began to show itself in the measured oxidation. With their further growth the oxygen consumption shot up, during the next 16 hours, to about 60 times the value of the chemical oxidation. The temperature was then raised to 51 deg. Cent. The result of this was to kill off or stop the activity of the existing *B. coli* organisms and lower the oxidation to about a sixteenth. Meanwhile, however, the spores of the thermophilic *B. Calfactor* began to develop; and in a few more hours the growth of this organism increased the oxidation about 90 times. Raising the temperature to 61 deg. Cent. caused only a limited diminution in the oxidation, as the *B. Calfactor* still flourishes fairly well at this temperature. But when the temperature was raised to 71 deg. Cent. there was an enormous fall in the oxidation rate, and the diminution continued still further, since all bacterial activity was suspended, and only the chemical oxidation, which decreases with time if the temperature is constant, was left. A further raising of the temperature to 81 deg. Cent. caused a temporary increase to double in the oxidation rate, and a similar result occurred on raising the temperature to 90 deg. Cent.

As regards the "chemical" oxidations at the higher temperatures, it should be remarked that they would almost certainly have been much higher if the hay had not already been exposed to oxygen for so long at the progressively rising temperatures.

Haldane and Makgill noted that hay which had been fermented by microorganisms had a greater absorptive power for oxygen than unfermented hay either in the dry or wet condition. This fact would indicate that fermentation had produced substances of a more easily oxidizable character. In the general discussion of their results Haldane and Makgill make the following interesting statement:

Although the spontaneous firing of a haystack is, like that of a mass of broken coal or other easily oxidisable material exposed to the action of oxygen, due to an oxidation process, the process, in the case of hay, has peculiar features owing to the initial co-operation of living organisms in the oxidation process. The experiments described above have shown, however, that there is no essential difference between the process in the haystack and in a mass of coal. The rapid development of heat in a large mass of damp hay is due almost entirely to the growth and activity of bacteria, of which one species raises the temperature to about 42 deg. Cent., while another species, which then begins to grow, can take the temperature to near 70 deg. Cent. Oxidation, however, occurs in the damp hay at ordinary temperatures at a limited rate even when bacterial action is absent; and a perfectly sterile haystack would be capable of spontaneous firing if it were large enough and were given sufficient time, just as any sufficiently large mass of broken coal is capable of spontaneous firing. As was pointed out by one of us in discussing the spontaneous firing of coal, the cumulative action of the heat carried forward by the air currents which establish themselves owing to convection (or to ventilation pressure in the case of gob fires), must inevitably lead to firing unless the heat produced can escape at such a rate as to stop indefinite rise of temperature.

The fact that haystacks do not spontaneously fire more frequently is in the long run due to their being of only moderate size. With stacks below a certain size the hay can never fire, since even if there is considerable heating from bacterial activity the heat produced by purely chemical activity at the temperature to which the bacteria have been able to raise the hay is too small to balance the loss of heat from the surface.

ENZYMIC-REDUCTION THEORY OF TSCHIRCH

The hypothesis of the formation of pyrophoric carbon by the dry distillation of hay at 70° C., as proposed by Mielche, was criticized by Tschirch (27) of the University of Bern in 1917. Tschirch at the same time advanced a new theory which is based upon the reaction of reducing enzymes. The following extract is translated from his article upon the subject (27, p. 133-137):

The combustion of hay destroys annually in Switzerland millions of value which might be saved to the country if there were some means of preventing these fires entirely or at least of checking them. A prerequisite for preventing the fires, however, is to know how they are produced. There has indeed been no lack of explanations. The explanations most generally accepted regard the cause as an accelerated intermolecular respiration in the interior of the still living plant cells which produces as a consequence an increase in temperature and thereby creates favorable conditions for the development of microorganisms. Respiration is thought to raise the temperature to 40° , and activity of microorganisms to 70° and more. At this temperature a "dry distillation" is then thought to take place which gives rise to a combustible gas and pyrophoric carbon and then to an ignition of the combustible gas. This explanation is manifestly wrong, as a simple consideration of the matter will show. Let us examine its arguments. By respiration in the plant physiological sense we mean a process opposite to assimilation as a result of which oxygen is consumed and carbon dioxide produced, in other words a gas is generated that has preeminently the property of preventing ignitions and of extinguishing fires. By dry distillation we understand a reduction process that is produced only far above 70° as a result of which materials are broken down in the closed retort to simple hydrocarbons of the aliphatic series, with a simultaneous reduction of carbon dioxide to carbon monoxide and a formation, by the red hot walls of the retort, of aromatic hydrocarbons by a process of ring closure. The temperature in the retorts of our illuminating gas factories exceeds 1000° . At no phase of the process is there any formation of pyrophoric carbon. Combustible gas can therefore not be produced in a haystack and if it is not produced it can consequently not ignite.

We are therefore compelled to abandon the above cited explanation and must look for another.

In connection with a study of the processes that take place in the drying of medicinal plants I have encountered a series of experiences which I would like to make the basis of a new "Haystack Theory." The fundamental reaction which takes place in a haystack that is heating and approaching a final state of ignition is an *intercellular enzymic reduction process* which involves, even at a moderate increase in temperature, the amino acids of the plasma as well as the saccharides of the tissues and cell contents and results in a splitting off of oxygen. A rapid evolution of oxygen has also been recognized in numerous other cases (I need only mention calcium chlorate explosion) as a cause of explosions and haystack fires are an exact picture of explosion fires.

Plant cells contain a complex of different enzymes, partially antagonistic,—oxydases, reductases, hydrolases, etc.—which either do not react at all, or only very slightly, (that is to say are in a state of inactivity) at ordinary temperature in the cells that have become low in water content as a result of drying out and which even in the cells of somewhat higher water content of half dried thinly spread hay exercise no special action at moderate temperature. (In this connection it should be remarked that the discoloration of grass when it is changed to hay is only partially due to enzymes and is to be attributed principally to the action of the acid juice of the cell upon the chlorophyll). If, however, half dried hay is packed tightly together in a thick layer, the most easily reacting oxydases (oxydation ferments or oxydizing enzymes) are the first to become active.

This first phase of the reaction is the first nondangerous stage that is associated with only a slight increase of temperature. It is an oxydation or combustion process that involves a consumption of oxygen. As soon as the oxygen is used up, however, the activity of the reductases (reduction ferments or reducing enzymes) sets in. They find points of attack in all the oxygen-containing constituents of the cell contents and cell membrane. In the cell contents they find the polypeptids of the richly albuminous plasma, which are built up of amino acids, that is to say structures of the type of aspartic acid $\text{COOHCH}_2\text{CHNH}_2\text{COOH}$. In the membranes, starch and sugar they find polysaccharids, highly oxygenated structures of the type of $\text{CH}_2\text{OH CHOHOH CHOHOH CHOH CHOHOH COH}$. Cellulose, for example, contains 51% and aspartic acid 48% oxygen. The reduction process which advances rapidly with rising temperature is the second dangerous stage which sets in about 50° – 70° . At these ranges of temperature the reductases apparently attain their optimum of activity. Very favorable conditions for their action exist especially in the interior of a haystack where all the oxygen is consumed by oxydases. The disintegration process reaches its maximum, therefore, in the interior of the haystack and can proceed here to complete carbonization, preceding which in a

preliminary stage, there are first produced brown colored intermediary products, that still contain H and O, and which also constitute the basis for the color of "brown hay". The abundant supply of oxygen, that is suddenly made available in the reduction process within the firmly packed haystack, where no outlet is possible for the generated gas, leads finally as in so many other cases to an explosion, that is to say to a rapid combustion of the available carbon compounds, both those reduced as well as those still unreduced. The heat that is generated in the reduction process cannot alone explain the ignition since this never mounts to the ignition temperature of cellulose. It is only the generation of oxygen and the occurrence of an explosion that explains satisfactorily the ignition.

That bacteria are concerned in the process which takes place in a heating haystack appears improbable. The course of the process does not indicate this. At any rate they play only a secondary rôle.

BURRI'S THEORY OF HEAT-RESISTING ENZYMES

In 1919 Burri (6), director of the Swiss Dairy and Bacteriological Station of Bern-Liebefeld, proposed a somewhat modified view of the enzymic theory of spontaneous heating. The following extract is translated from his article (6, p. 30-32):

That hay or other plant material of low water content can undergo spontaneously in the presence of oxygen an increase in temperature from, say, 45° to 70° C. as the result of a simple oxidation process, intensified subsequently by catalytic agents, appears in the first place highly improbable. In the next place we observe that in the processes of spontaneous heating, and especially with hay, the temperature frequently exceeds 70° and reaches limits in which the life of microorganisms or the activity of the usually very delicate enzymes, whether of microbial or plant cellular origin, is absolutely excluded. If now with the exclusion of biochemical factors temperatures of 80°, 90° and more can be reached in haystacks, in which only purely chemical heat sources could be involved, then the view appears plausible that these same sources are already active at lower temperatures, as between 50° and 70°. This idea is in conformity with the previously mentioned oxidation experiments of Boekhout and de Vries upon hay and tobacco leaves in closed glass tubes. The fact that the temperature inside of the large heaps of tobacco leaves, such as are seen in industrial use, can rise to 60° and more without there being any detectible important development of microorganisms, may also be pointed out in favor of an oxidation process, unless one excludes the idea that the respiration enzymes are still active at higher temperatures than is ordinarily supposed. The latter possibility will be referred to again later. If Mische shows that sterilized hay is not capable of spontaneous heating, that is not a sufficient proof that chemical oxidation processes do not play any rôle in temperature ranges of 50° to 70° since the sterilization process might produce changes in the plant that are unfavorable to subsequent oxidation.

Briefly it can be said that good reasons exist for the view that in hay which is sufficiently wet, after excluding the heat of plant respiration, a further increase in temperature can be produced by a chemical oxidation process. Whether the intensity and duration of this process would be sufficient to introduce the third undoubtedly purely chemical heat-production phase of 70° C. and upwards remains an open question although it seems improbable.

At least the microbiological theory is as convincing as the oxidation theory for explaining the temperature increase from 45° to 70° C. According to this theory, which at present seems to have the preference, the heat produced by respiration and subsequently by the bacteria whose growth-optimum lies around 40° gives rise to conditions for the development of the thermophilic microorganisms which because of their adaptation to high temperatures flourish best between 40° and 70° and are therefore in position by their action upon various substances to produce perceptible amounts of heat. As already mentioned the *Bacillus calfactor* according to Mische's investigations is thought to be especially active in hay and to be able to raise the heat from 45° to 70°. This view however is not yet definitely established. There are lacking, for example, in the cases of spontaneous heating communicated in Mische's work, continuous quantitative bacteriological tests from which it can be concluded that a causative connection exists as stated between increase in number of organisms and increase in temperature. It must be considered also that the simultaneous

occurrence of the three factors, nutrients, warmth and moisture produces under all conditions a more or less luxuriant bacterial vegetation, a condition that can easily give rise to a confusion of cause and effect. We have seen in the case of tobacco that a marked temperature increase (up to 60°) can result without any apparently noticeable development of bacteria. The same causes could be operated in hay as in tobacco, while in addition a somewhat higher moisture content might favor perhaps a certain microflora, which in this case should be regarded not as the cause but as the result of the warmth.

Now with regard to the enzymatic theory of spontaneous heating, this at first sight has something enticing, at least so far as the oxidizing enzymes are concerned. These latter may be identified, without further argument, with the respiration enzymes and I am inclined to attach a greater importance to them for spontaneous heating than has generally been done, and especially upon the basis of the following argument.

The experiments conducted by plant physiologists upon the course of respiration at higher temperatures have showed that with increasing temperature the respiration becomes more and more intense, until it ceases quite suddenly at a temperature that lies between 45° and 50° C. which thus indicates the death of the plant. We know, however, that enzymes are not equally sensitive under all conditions and this is especially true if they occur in tissues that have a relatively low water content. Certain plant seeds, for example, which we know also respire, can be heated to 100° and over without losing their germinating power. In this case the lower water content of the material protects the enzymes against the injurious action of a high heat. In a similar way perhaps the moderate drying of grasses and plants, customary in hay making, might put the enzymes that they contain into a more resistant, although less active, condition which would have the result that the process of heat formation resulting from respiration would become quiescent not at 45° or 50° but perhaps at 60° C. or higher. In case this supposition should be correct, there would then be the possibility that the increase in heat might lead, without the cooperation of bacteria, to a temperature level where purely chemical and physical processes would be able to take over the process of further heat-production. I would like to give an enzymic theory of spontaneous heating, modified in the manner just indicated, equal consideration with the oxidation and microbiological theory. On the other hand I am unable to accept the hypothesis proposed by Tschirch that in the especially important temperature range of 50° to 70° C. reduction enzymes play the important part. In the first place it would be pertinent to remark that the biochemical reduction processes which take place in a lack of oxygen with plant cells such as microorganisms, would be able to liberate only moderate amounts of heat and that therefore an actual spontaneous heating could hardly develop. In the second place it can be stated that in such processes, at least so far as I am aware, molecular oxygen is not produced but the oxygen undergoes a change of grouping with other elements of certain molecules as a general result of which the larger molecules are split into smaller ones. The latter are partly less and partly more strongly oxidized than the unsplit molecule. To the most abundant highly-oxidized products of a metabolism, that takes place without the participation of free oxygen, belong the simple carbon acids and carbon dioxide. In agreement with this view the plant masses which have been subjected to spontaneous heating always contain considerable amounts of free acids, and so far as the gases contained in the interior of such heated masses have been examined up to the present time, carbonic acid has been found in excess with oxygen and nitrogen,—the oxygen as a matter of fact in smaller amount than corresponds to the relation of oxygen to nitrogen in the air. The amount of oxygen found is obviously only the remaining atmospheric oxygen that has not yet been used for oxidations.

HILDEBRANDT'S CRITICISMS OF THE ENZYMIC THEORIES

The enzymic theory of spontaneous heating as proposed by Tschirch and later modified by Burri has recently been contested in an important paper by Hildebrandt (13, p. 483-484) from whose work the following paragraphs are translated:

In my experiments I was able to confirm again the discovery made previously by Cohn (1893) and by Miebe (1907), that in sterilized material, which was

incapable of spontaneous heating, an inoculation with microorganisms could elevate the temperature far beyond 50°, as soon as these forms of life could multiply sufficiently in this substance. This observation alone did not make it possible, however, to draw any direct conclusion as to the cause of the spontaneous heating of hay; especially the question as to the heat producing activity of plant enzymes remained unexplained. Since I experimented only with dead hay only the post-mortal acting respiration enzymes of the hay itself or the excreted enzymes of the microflora are involved in any such production of heat. I therefore attempted to find an experimental answer to the question.

If the water content of the hay was so regulated that the development of the organism flora was just excluded, then the capacity for spontaneous heating was also prevented. The treatment of the hay with different antiseptics which so far as could be determined suppressed the organisms but not the enzymes produced the same results. Also the addition of a germ-free oxydase-containing pressed juice into the sterile hay caused no increase in temperature (I have already explained in Chapter I how Tschirch and Burri attribute the initial stage of spontaneous heating to the activity of oxydases). On the other hand old meadow hay underwent heating in a perfectly normal way although after carefully rubbing with a little water in a mortar it showed not the slightest oxydase reaction while fresh grass and potato sprouts, for example, gave a distinct positive reaction with the test.

These experiments did not give any support to the theory of heat production by the activity of oxydases. That Tschirch's view of a further development of heat beyond 45°-50° by the action of reductases is untenable I believe to have shown in my previous experiment No. 9. This experiment had for its original purpose only the establishment of an estimate of the oxygen consumption of a mass of hay in an active state of spontaneous heating and it showed that the supply of oxygen in a 0.1 cubic meter bell jar was already completely used up at 47° C. If the Tschirch hypothesis were then correct, the activity of the reductases after consumption of all the oxygen should have set in at 47° C. without fail and the heating should have at least gone to the temperature (63½°) obtained experimentally under normal conditions. Likewise experiment 17d. in which an addition of possibly occurring microbial enzymes was tried upon sterile hay, gave a negative result. Spontaneous heating could not be produced.

The experiments that were undertaken showed without exception that a separation of spontaneous heating and microbial life was impossible. A completely decisive answer as to the causes of spontaneous heating can, however, not yet be given notwithstanding the complete agreement of the experiments. There still remains especially the objection that not only the organisms but also the plant enzymes were checked by the disinfection that was used, or that in the addition of the expressed plant juice to sterile hay the enzymes did not reach the hay in an active condition. An absolutely definite experimental answer to the question of whether microorganisms or enzymes are the producers of spontaneous heating can be given only when it is possible to obtain successfully a sufficient quantity of a pure cultural extract (material that is free from microorganisms) of the higher plants and then to investigate this, after the cessation of all life in the hay, with respect to gas exchange and after germ-free packing with respect to capacity for spontaneous heating.

Meanwhile the defenders of the enzymic theories of spontaneous heating must for a long time bear the burden of proving convincingly the correctness of their views. So far as can be determined experimentally everything indicates with the highest degree of probability that the spontaneous heating of hay is due to the metabolic activities of microorganisms.

THE CATALYTIC OXIDATION THEORY OF BOEKHOUT AND DE VRIES

As the result of a long series of investigations upon the heating of hay and tobacco, Boekhout and De Vries (3) of the Agricultural Experiment Station of Hoorn, Holland, conclude that microorganisms play no part in the phenomenon, which they attribute to purely oxidative chemical processes. Their theory is based upon the supposition that—

the chemical exothermic decompositions which produce this phenomenon owe their origin to the interaction of substances that occur in the cell juice, proto-

plasm and cell wall of plants, that is to say substances that exist already formed or that arise during the drying of the grass as a result of intermolecular respiration or other cause. Unfortunately the experiments that were undertaken with the purpose of identifying these substances did not lead to the desired result. Neither treatment with water nor with 2 per cent alkali solution nor with the 3 per cent hydrochloric acid could effect a separation of groups of bodies that were capable of chemical inter-reaction. (3, v. 21, p. 398.)

As a result of further investigations upon the subject Boekhout and De Vries came to the conclusion that—

the spontaneous heating of hay is an oxidation process in which the iron that occurs naturally in the plant acts as a catalyzer. The part which water plays in the process is (1) that of converting the pentosans and nitrogen free extracts into a state of easy oxidizability and (2) that of causing a dissociation of the iron compounds with a greater production of free iron-ions that intensify the catalysis. In accordance with this view any cause that produces an increase in the iron content of the plant gives rise to a predisposition on the part of the hay obtained therefrom to undergo spontaneous heating. (3, v. 21, p. 407.)

That the pentosans of hay are particularly subject to oxidation was demonstrated, according to Boekhout and De Vries (3, v. 44, p. 303), by the fact that furfural could be detected in the gaseous products obtained from the fermenting hay.

LAUPPER'S THEORY OF PYROPHORIC IRON

In 1917 Laupper (17), a chemist of Zurich, Switzerland, who has probably observed more actual occurrences of the spontaneous combustion of hay than has any other student of the subject, made the announcement that it was not pyrophoric carbon which caused hay to ignite spontaneously, as had hitherto been supposed, but pyrophoric iron. By treating pyrophoric carbon prepared from hay according to Ranke's method with concentrated hydrochloric acid in order to remove all occluded iron particles and then heating the washed residue to redness in a test tube, Laupper found that the carbon had lost its pyrophoric properties. If, however, the extracted carbon be moistened with a solution of an iron salt and again heated, the original pyrophoric quality is regained, the process being similar to the production of pyrophoric iron by heating iron oxalate. The conclusion was therefore formed that it was pyrophoric iron and not pyrophoric carbon which caused the carbonized hay to ignite. Later experiments by Laupper showed, however, that the iron which occurs naturally in hay in organic or inorganic combination is not rendered pyrophoric except at a temperature of about 280° C. The problem of explaining the elevation in temperature between the 70° or 80° which marks the termination of biological processes in the hay and the 280° required for spontaneous ignition was, therefore, no nearer solution than before. Laupper was therefore induced to subject the so-called haystack problem to another critical study, the results of which are contained in an exhaustive report with historical introduction and very full bibliography in the *Landwirtschaftliches Jahrbuch der Schweiz* for 1920 (17, p. 1-54). The following schematic diagram (Table 2) gives a summary of Laupper's conclusions with regard to the supposed development of the chemical changes that take place in the spontaneous heating of hay between 20° and 340° C.

TABLE 2.—Schematic diagram (Laupper) showing the supposed development of chemical changes during the spontaneous heating of hay based upon the conclusions of observations and laboratory experiments

Temperature (° C.)	Processes in spontaneous heating of well dried hay	Decomposition products	Exothermic reactions	Character of changes
20 to 35.....	Stimulation of respiration activity as result of bruising plant tissues which is especially produced by treading hay. Activation of oxydases by production of water and commencement of the catalytic action of the oxydases. First decomposition and commencement of sweating.	Carbon dioxide water vapor.	Strong.....	Physiological, colloidal chemical and catalytic.
35 to 45.....	Commencement of weak carbonization of sugar (hay heated in test tube with water to 40° to 50° C. is colored brown). Death of the plant cells at 45° (?).	Caramel water vapor.....	Weaker.....	Catalytical and chemical.
45 to 70 ¹	Combined action of plant respiration and synaeresis (splitting off of water from hydrated colloids). Strong vaporization; odor still aromatic. Commencement of evolution of ammonia, formic acid, etc. Constant advancement of exothermic decomposition.	Ammonia water vapor alcohol.	Again stronger.....	Do.
60 to 70.....	Swelling of blades of hay by action of heat, pressure and water vapor. Important moment for hastening of the exothermic reaction.	Rapidly increasing chemical processes intensified by the accumulation of warmth in the hot pocket.	Chemical.
70 to 90 ¹	Formation of "brown hay." Decomposition of pectins. Irritating (not burnt) odor. Commencement of water distillation. Increasing intensity of chemical reactions.	Formic acid acetic acid.....	do.....	Do.
90 to 100.....	Water distillation rapid. First decomposition of proteins. Splitting off of chemically bound water from carbohydrates. Rapid carbonization of sugar in presence of ammonia. Caking of hay.	Hydrogen sulphide I; furfural I.	Temperature temporarily stationary.	Wet distillation important point of chemical reactions. Between 90 to 100° temperature remains stationary but evaporation increases.
100 to 110 ²	More extended period of stationary temperature. Distilling off of water.....	Transition to dry distillation.
110 to 170 ⁴	Drying out of caked hay and concentration of its content of distilled and sublimed decomposition products. Formation of HNO ₃ by oxidation of NH ₃ .	Ammonium nitrate.....	Dry distillation; violent chemical reactions.
170 to 250.....	Strong progressive continuance of the exothermic reactions and rapid increase of temperature.	Rapid increase of temperature.	Do.
250 to 280 ⁵	Decomposition of cellulose carbohydrates. Decomposition of proteins.....	Hydrogen sulphide II; furfural II; splitting off of water as vapor.	do.....	Do.
300.....	Stage of possibility of ignition from access of oxygen.....	Disappearance of water and furfural.	Ignition.....	Do.
320 to 340.....	Decomposition of last carbohydrates, etc.....	Furfural III; pyrophoric manganese.	do.....	Do.

¹ 70° = Point of warning.

² 90° = Critical point. Danger of sudden increase in temperature.

³ 110° = I. Possibility of explosion (NH₃+O) of fermentation or carbonization gases.

⁴ 170° = II. Possibility of explosion (NH₄NO₃+caramel carbon).

⁵ 280° = Danger of ignition (pyrophoric iron).

The temperatures noted in Laupper's diagram pertain only in the very lowest ranges to the haystack as a whole, whereas those in the higher ranges are confined entirely to a very localized section of the stack, the so-called hot pocket, fire pocket, or combustion chamber (Wärmekammer, Brandherd, etc.), which is the principal seat of chemical activities. The first requisite for the formation of such hot pockets is thorough insulation, and this is furnished most effectively by the hay itself, which, when forked into mows or stacks, forms regular compact layers that prevent the escape of heat by radiation. Even when apparently dry, hay contains a considerable quantity of moisture, and the still-living plant cells, especially when the grassy tissues have been crushed or bruised by stamping or treading, begin to develop heat by respiration, oxygen being absorbed and carbon dioxide evolved.

The heat that is generated by plant respiration and the activity of microorganisms displaces a considerable quantity of moisture that condenses in the overlying strata of hay, making the hay soft, dissolving the soluble carbohydrates, pectins, gums, and albuminous materials, and cementing the whole layer into a compact nonconducting cake (Laupper's heufladen), which acts as a very efficient insulator to the heat that is being generated in the pocket underneath. Ammonia, formic acid, and other volatile products begin to be evolved, and the sugars start to carbonize as a result of the action of the ammonia in the presence of heat, with splitting off of chemically combined water. Chemical reactions are now intensified in the hot pocket, and as the temperature approaches 100°C . there is a rapid distillation of water, the consumption of heat for this purpose causing the temperature to remain quiescent for a time. When most of the moisture is expelled from the hot pocket, the temperature begins to rise rapidly again in consequence of the accelerated exothermic processes, with the result that a destructive dry distillation and carbonization of the hay begins, the hot pocket now approaching the character of a fire pocket.

Laupper calls particular attention to the presence of nitrates in the caked hay that surrounds the hot pockets. He found that the nitrates occurring naturally in hay are destroyed in the preliminary process of sweating and that the 1.5 per cent or more of combined nitric acid in caked hay must therefore have been produced by a synthetic process. He explained that this result was brought about by the oxidation of the ammonia (distilled from decomposing nitrogenous substances) in the presence of free oxygen that is simultaneously evolved. Laupper found upon heating dry nitrate-free hay in a combustion tube through which oxygen and ammonia were conducted that the two gases united with explosive violence with production of nitric acid. Laupper attributes the formation of the crystals of ammonium nitrate, which he isolated from caked hay, and also some of the explosives observed in haystack fires, to this reaction. The presence of flammable gases of fermentation, or destructive distillation, origin might also contribute to such explosions and fires. Laupper indicates 110°C . as the first danger point of explosion and 170° , the observed temperature of the explosive ignition of a mixture of ammonium nitrate and hay carbon, as the second danger point.

Laupper demonstrated the possibility of a violent exothermic reaction at this stage of the heating process by heating wet hay, with which a little ammonium nitrate and glucose had been mixed, in a hot air oven at 150° C. Under these conditions when the hay approached 150°, the temperature shot up suddenly, in a few seconds reaching 350°. The carbonaceous residue ignited spontaneously, after breaking the flask in which the reaction was conducted. This ignition was attributed by Laupper to pyrophoric iron, which was

estimated to be formed at 280°—the third danger point of spontaneous combustion.

According to Laupper, the heat that is developed in the fire pocket or combustion chamber as a result of the increasing intensity of the chemical reactions causes the evolved gases to exert a strong pressure upon the surrounding walls of caked hay. "Chimneys" or "smoke channels" are forced out from the fire pocket into the surrounding hay in various directions, these openings following the paths of least resistance until they approach the surface of the stack or mow. (Figs. 3 and 4.)

The escaping odor of burnt hay, noted in



FIGURE 3.—Fire flue in a haystack partly destroyed by spontaneous combustion. After Laupper (*IS, Tafel II*)

Ranke's account, is usually the first indication of impending disaster. Finally, when one of the smoke channels reaches the surface, there is an inrush of air, and upon contact of the pyrophoric iron with oxygen ignition takes place. An explosion of carbon monoxide (with blue flame) and of other flammable gases follows, the discharge of flames through the various smoke channels setting fire to the whole stack with the great rapidity that is characteristic of the spontaneous combustion of haymows.

Such, in outline, is the theory of the spontaneous combustion of hay as developed in Switzerland by Laupper as a result of laboratory investigations and of many critical examinations of haystacks and haymows that were either in a state of heating or of actual combustion.

DIVERGENCE OF OPINIONS

The extracts that have been quoted from the very voluminous literature upon the spontaneous combustion of hay are sufficient to indicate not only the complexity of the problem but also the extreme divergence of opinions upon the subject. Scarcely any topic in chemical literature is in a more controversial state. In the passages selected for quotation there are theories of ignition by gas condensation versus theories of ignition by pyrophoresis, of pyrophoric carbon versus pyrophoric iron, of bacterial heat versus enzymic heat versus chemical heat, of oxidases versus reductases, of wet distillation versus dry distillation, of carbonization at high temperature versus carbonization at low temperature, of flammable gas versus nonflammable gas. Examples of such contradictions of opinion can be greatly multiplied, and the student of the subject finds himself helpless when he attempts to strike a satisfactory balance between the various opposing views.

NEW SUGGESTIONS AS TO THE CAUSE OF THE SPONTANEOUS COMBUSTION OF HAY

In the remainder of this bulletin the writer will make an attempt to develop a theory for the spontaneous combustion of hay which, if it does not solve the problem, may provide at least a clue to its final solution.

FACTORS IN THE SPONTANEOUS IGNITION OF OIL-COATED COTTON

The clue proposed is a departure from the ordinary method of approach and, with the elimination for the present of all the complex variables that exist in a fermenting haystack, consists in confining attention at first to some of the factors involved in the more simple, purely chemical example of the spontaneous ignition of a wad of oil-soaked cotton. The production of fires from the spontaneous ignition of cotton waste that has been used by painters for wiping up linseed oil is a familiar occurrence. In this case the cotton serves as a porous

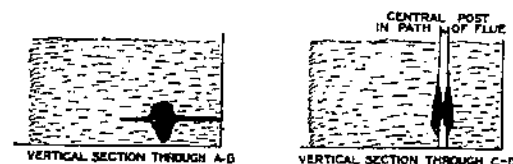
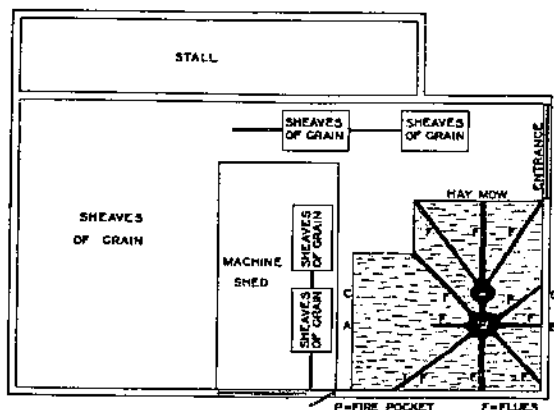


FIGURE 4.—Plan of haymow damaged by spontaneous combustion at Duebendorf, Switzerland, July 25, 1920, showing location of fire pocket and flues. After Laupfer (18, p. 132)

combustible vehicle that gives the adhering films of unsaturated oil the most favorable opportunity for combining with atmospheric oxygen, the outer fibrous layers of the wad serving also as an insulating material for the retention of the heat that is continuously generated in the interior of the mass.

Without going too deeply into the chemistry of this reaction it may be assumed that there is first an absorption of molecular oxygen from the air at the easily broken points of unsaturation in the oil molecules with the formation at first of fatty peroxides.³ The latter

then decompose in the presence of moisture into hydroxy compounds and atomic oxygen that from its intensive combining power may form either hydrogen peroxide or exert directly an energetic oxidizing effect upon the organic matter with which it comes in contact. As heat begins to develop, the speed of the reaction slowly increases until finally when the temperature has reached a point in the neighborhood of 100° C., the constantly accelerating oxidation raises the temperature of the oil-coated cotton very rapidly to the point of ignition.

The curve in Figure 5 shows the course of an unpublished experiment by E. J. Hoffman,⁴ in which 50 grams of cotton waste coated

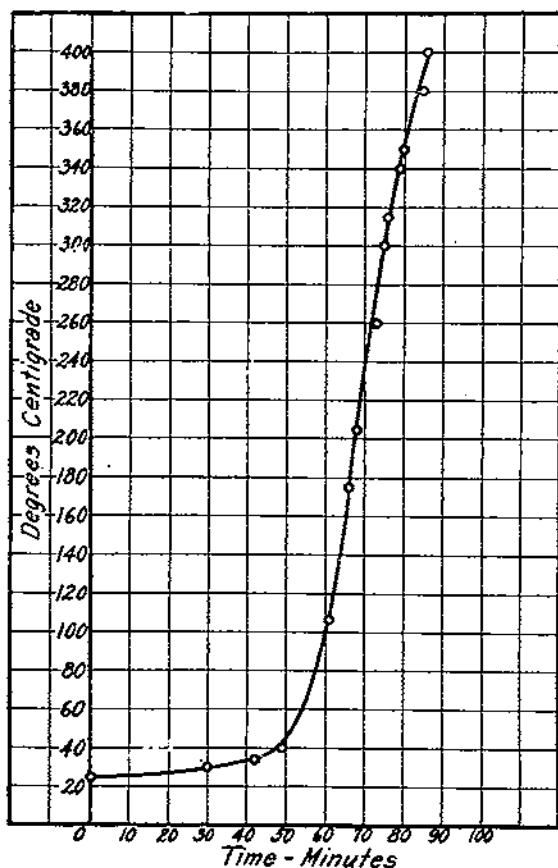


FIGURE 5.—Curve showing temperature increase in oil-coated cotton waste

with a mixture of 50 grams of raw linseed oil and 5 grams of a linseed-oil solution of cobalt oleate (approximately 0.1 gram cobalt) was placed loosely in a wire basket 5 inches deep and 3¼ inches in diameter. The basket was set on an iron tripod indoors under a hood with the bulb of a thermometer about 2 inches below the top surface of the mass. In 30 minutes the temperature had risen

³ See article by Browne (5) for a discussion of the theories of the oxidation of unsaturated fats. See article by Tschirch and Barben (23) on the existence of fatty peroxides and hydrogen peroxide in oxidized fats.

⁴ Chemist in the chemical engineering division of the Bureau of Chemistry and Soils engaged in research on farm fires.

from 25° to 30° C., in 49 minutes to 40°, in 60 minutes to 100°, in 73 minutes to 260°, and in 86 minutes to 400°. When a gentle air blast was applied to the mass at 400°, the oil-covered cotton burst into flame.

The spontaneous heating of linseed and other unsaturated oils spread upon cotton has recently been subjected to a critical study by Thompson (25) of the Factory Mutual Laboratories of Boston, in a Mackey testing apparatus. It was demonstrated that spontaneous heating was favored by increasing the humidity up to the point where the cotton carried about 10 per cent of water. Thompson also showed very strikingly that the spontaneous heating of oily waste was greatly accelerated by the products formed during the oxidation, a sample of oiled cotton, for example, which had been heated and cooled off, showing a much greater initial heating rate than a freshly prepared sample at the same temperature. This effect is very probably owing to fatty peroxides previously formed. Thompson also observed that the presence of metallic oxides, such as ordinary iron rust, had a catalytic effect in hastening the process of spontaneous heating, which was probably similar to that of the cobalt oleate in Hoffman's experiment.

OXIDIZABLE, UNSTABLE, FERMENTATION PRODUCTS AS A CAUSE OF SPONTANEOUS HEATING

The theory of the spontaneous heating and ignition of large masses of hay that the author proposes is based upon the preliminary production by microorganisms under more or less perfect anaerobic conditions of unsaturated, highly unstable, intermediate-fermentation products upon the surfaces of the porous, cellular materials (the condition being therefore similar to that of the oil-coated cotton). The duration of existence of these readily oxidizable fermentation products is dependent upon the quantity of air that can gain access to the fermenting mass of hay and also upon the quantity of moisture which is present to serve as a reacting medium. If the heaps are small or of open, loose structure the intermediary compounds are destroyed almost as soon as formed, with the result that when vegetative microorganic life is all destroyed at 70° to 80° C., there is not a sufficient residue of such easily oxidizable, unsaturated substances to carry the production of heat to higher limits. The heat of the microbial life period is probably owing in large part to the oxidation of the same intermediary unstable products that participate in the elevation of temperature above 80°, so that the supposition indicated by Burri (although upon a different basis) is undoubtedly correct. For example, "if temperatures of 80°, 90° and more can be reached in haystacks, in which only purely chemical heat sources could be involved, then the view appears plausible that these same sources are already active at lower temperatures, as between 50° and 70°." According to this view there is then no difference in the character of the heat production between 50° and 70° and that between 70° and 150° or upwards, the entire range of heat production being thus due to purely chemical causes. In other words, the microorganisms simply produce the highly unstable compounds whose subsequent oxidation, like that of the unsaturated oil upon cotton, generates the increasing quantities of heat that lead first to the destruction of the organisms

themselves and then eventually to the ignition of the hay. The rapid oxidation of such intermediary unstable compounds would explain the high oxygen absorption and high carbon dioxide production that Haldane and Makgill obtained in their experiments with moist hay at 60°. The subsequent rapid falling off in oxygen absorption and carbon dioxide production noted by these observers is simply the indication that the formation of these easily oxidizable compounds has come to an end.

The foregoing explanation of the spontaneous combustion of hay may be criticized on the grounds that there is no evidence for the existence of such highly unstable intermediary compounds as this hypothesis requires. The difficulty in the experimental search for such compounds is that in the drawing and manipulation of hay samples from a fermenting pile the highly unstable substances are unavoidably exposed to the air so that they are oxidized and destroyed before the chemical examination can be completed. It is possible, however, to duplicate in the laboratory some of the conditions existing in a hay pile for the formation of such unsaturated compounds and, by adopting suitable means for preventing access of oxygen, to effect their separation and identification.

EXPERIMENTAL PRODUCTION OF UNSTABLE, UNSATURATED COMPOUNDS FROM SUGAR

One of the most common observations made in the examination of agricultural products undergoing spontaneous heating, such as horse manure, and hays of various kinds, especially clover and alfalfa hay, is that ammonia is produced. Boerhaave, Cohn, Miele, Lauppper, and many other authorities call attention to the evolution of ammonia from hay that is undergoing spontaneous heating and to the alkaline condition that is produced thereby.⁵ Plant sugars in dilute alkaline solution at a moderately warm temperature undergo interesting changes, especially in the absence of atmospheric oxygen. Considerable uncertainty still exists concerning the nature of the first compounds produced in the breaking down of the simple hexose sugars by dilute alkalies. Numerous unsaturated compounds of a highly unstable reactive character are among the substances formed as may be demonstrated by the following simple experiment.

If a 1 per cent aqueous glucose solution is treated at 67° C. with one-half per cent of CaO (completely slaked in water) in a flask from which the air is excluded, the solution turns a yellowish brown, and a copious flocculent precipitate soon forms. After settling, the precipitate is filtered upon a Buchner funnel, washed with dilute milk of lime solution and then with alcohol and ether, being always covered with liquid to prevent oxidation. It is then transferred as rapidly as possible to a vacuum desiccator, from which the air is immediately exhausted. If, after partly drying, a little of the moist, white precipitate be stirred, in a beaker exposed to the air, with the bulb end of a thermometer a considerable darkening in color with a rapid rise of temperature (20° to 48° C.) will be noted. Oxygen is rapidly absorbed, as can be seen when the crumbled, moist precipi-

⁵ Berthelot (2), contrary to most other observers, reported the absence of ammonia in his experiments upon the gases produced by the fermentation of hay.

tate is placed in a flask of this gas attached to a eudiometer tube. If the lime precipitate be decomposed with dilute sulphuric acid and then extracted with ether a crystalline highly unstable compound is obtained upon evaporation of the solvent. This compound, which reduces silver nitrate and Fehling's solution instantly in the cold, is found to be highly unsaturated, as shown by the avidity with which it absorbs bromine, iodine, and hydrogen. Elementary analysis and molecular weight determinations show it to have the formula $C_6H_8O_5$ with the probable structure of $CHOH:CHCOOH$, which is hydroxyacrylic or glucic acid.⁶ The compound readily decomposes into formic acid with polymerization into complex substances of an unknown character. It undergoes a partial sublimation at the temperature of boiling water, and a compound of this character, if formed in the interior of a fermenting hay pile, might be distilled in the absence of oxygen from the region of a hot pocket to a cooler part of the stack. The possible bearing of a dry distillation at comparatively low temperatures upon special phases of the haystack problem is therefore not to be wholly excluded from consideration. The production of formic acid by the breaking down of hydroxyacrylic acid is a possible explanation of the presence of formic acid in the irritating gaseous emanations from very hot fermenting hay. (See Table 2 for temperatures 45° to 70° and 70° to 90° .)

The formation of easily oxidizable unsaturated compounds similar to, although not necessarily identical with, hydroxyacrylic acid, would appear to be highly probable under the complex anaerobic conditions that exist in the interior of a fermenting haystack where higher saccharides and proteins are broken down and where the hydrolytic products of these (sugars, amino acids, ammonia, etc.) undergo at a most favorable temperature numerous reactions among themselves and also various decompositions as a result of micro-organic activity. The process that has been sketched for the production of hydroxyacrylic acid is only one of numerous possibilities for the determination of which there is need of extensive research.

The supposition that a weakly alkaline medium, such as would be produced by the evolution of ammonia⁷ in the fermentation of vegetable proteins, amino acids, etc., facilitates the conversion of reducing sugars into the easily oxidizable substances that give rise to spontaneous heating, finds a certain confirmation in the fact that the hays which are the richest in nitrogenous substances, such as clover and alfalfa, are the most likely to undergo spontaneous combustion. This is especially true of the alfalfa meal-molasses mixtures (rich in both sugars and ammonia-producing ingredients) that are so extensively used for cattle-feeds and the frequent spontaneous combustion of which in warehouses, freight cars, etc., has caused fire insurance and transportation companies to regard the handling of such materials as a great risk. Haylike materials, on the other hand, that

⁶ See article by Nelson and Browne (22) for further information pertaining to this compound.

⁷ In a paper upon Microbial Thermogenesis by James Rettger, and Thom (16, p. 137) attention is called to the rapid production of ammonia during the spontaneous heating of cracked corn after inoculation with a pure culture of an actively thermogenic *B. subtilis* strain. The quantity of ammonia-nitrogen obtained from the corn before heating began was 0.91 mg. per 115 gms. of corn. This quantity had increased in 36 hours after heating to 7.00 mg., in 40 hours to 12.00 mg., in 65 hours to 17.73 mg., and in 85 hours to 21.80 mg.

are deficient in sugars and proteins, such as straw, are very rarely susceptible to spontaneous combustion.

RATE OF OXIDATION IN FERMENTING HAY

The prophecy was made by Miede that the temperature of an undisturbed haystack from which air was excluded would never be found in any place to exceed 70° or 80° C. Miede (21, p. 21) demonstrated the fact that damp hay in a container from which all oxygen had been displaced by hydrogen underwent no increase whatever in temperature. Hildebrandt (12, p. 450) showed that 300 grams of dry hay wet with 200 cubic centimeters of water in a Dewar flask when placed in a tightly closed bell jar of about 100 liters capacity underwent an increase of temperature in four days from 23° to 47°, when the process came to a standstill, all the oxygen having been consumed and the bell jar being completely filled with carbon dioxide. Upon the removal of the Dewar flask to the outside air the temperature in three days increased from 43° to 62°, which indicates a rapid penetration of atmospheric oxygen under conditions that were not the most favorable. Hildebrandt estimates that for the attainment of this temperature from 30 to 34 liters of oxygen were consumed by the 300 grams of hay.

It must be recognized that in a mass of such loose structure as a pile of hay the outside air can penetrate through the interstices between the stems and blades for a long distance into the interior so that oxidations can take place in a considerable zone in the region immediately surrounding the center of heat production. A small quantity of oxygen also undoubtedly diffuses through the compact cakey mass of hay that acts as an insulating wall about the so-called hot pocket where chemical activity is the most active. The oxygen penetrating in this way combines energetically with the unsaturated substances produced by microorganisms, thus giving rise to additional quantities of heat, but the supply is not sufficient to produce ignition until a disruption of the cakey wall at some point by the pressure of internal gases permits an inrush of air that is sufficient to hasten the oxidation of the hot material to the point of ignition. No doubt it frequently happens that the oxidation of the unstable fermentation compounds is gradually completed before ignition sets in, in which case the haystack begins slowly to cool and the danger of spontaneous combustion is past, a cake of partly carbonized hay remaining in the interior of the stack to tell the story of an escape from disaster.

Sufficient aeration of all parts of a stack of hay at the early stages of fermentation has been suggested as the best means for stopping the process of spontaneous combustion, and, in view of the oxidation of the unstable heat-producing compounds before the zones of bacterial activity have become too warm and dry, such a procedure is perfectly sound in theory. If the aeration is performed at an advanced stage of heating, however, the procedure is attended with great risk as is indicated by the experiences of Ranke and others.

VARIATIONS OF MOISTURE CONTENT IN FERMENTING HAY

It has not been found possible to effect the spontaneous combustion of hay in small laboratory experiments for the probable reason that

the exact condition of moisture content that is most favorable for the development of the phenomenon did not exist or there was an insufficient supply of the easily oxidizable fermentation compounds to produce the necessary heat.

The range of moisture content in hay at which spontaneous ignition can take place is probably within somewhat narrow limits. If the moisture content is too high the heat is used up in the evaporation of water; if the moisture content is too low the course of the final rapid heat-producing reaction is retarded. Thus Thompson found that a moisture content of 10 per cent was more favorable than smaller quantities for the spontaneous heating of oiled cotton. In a large stack of hay or in a large pile of manure there is a much better opportunity for a wide range of moisture content in different parts of the pile and hence a much better chance of obtaining somewhere the exact conditions necessary for spontaneous ignition than exists in a smaller mass of material.

It must also be recognized, as Laupper and others have pointed out, that spontaneous combustion may take place in hay that apparently has been well cured and put in the barn or stack in a uniformly dry condition. In such a pile of material a displacement of moisture from the warmer to the cooler parts of the mass begins at once, with the result that local zones of higher moisture content are produced, and then begin to heat. The whole pile of hay is thus thrown into a state of very unequal moisture distribution with some parts overmoist and others overdry but with an intermediate zone at some point where the conditions of moisture content, temperature, presence of oxidizable decomposition products, catalytic agents, and insulation are exactly right for rapid oxidation and spontaneous ignition.

SPONTANEOUS IGNITION OF HORSE MANURE AT ARLINGTON, VA.

The greater opportunity for spontaneous ignition in a large mass of fermenting material was made apparent more than three years ago by some troublesome fires that broke out in a pile of horse manure on the Department of Agriculture farm at Arlington, Va., of which the following account is given by James, Bidwell, and McKinney (14).

The observations reported in this paper were made upon a large pile of stable manure and straw at the Arlington Experiment Farm, Rosslyn, Va. Manure for fertilizer purposes had been hauled from a neighboring cavalry station and placed on the farm grounds in an open plot. As the manure was unloaded the horses and wagons were driven over the pile, and the load was deposited on the top. The custom had been to "cure" the manure from one to three years before spreading it. The first loads had been deposited some two and one-half years before, and the mass had grown to a pile about 200 feet long, 50 feet wide, and from 1 to 20 feet high. (Fig. 1.) Moderate heating of the manure had been accepted as an essential part of the curing, though fire had not formerly occurred.

Before September 9, 1925, the date of the outbreak, the weather had been warm, ranging from 87 to 95° F. There had been no heavy rains for two weeks. Daily additions had been made to the pile, and, although the mass was known to be excessively hot, the condition was not considered dangerous. Fire broke out during the night of September 9, and was discovered by the night watchman. The flames quickly spread over the entire west side of the long pile. Water was applied from pails, and the flames were extinguished. Within a few hours, fire again broke out along the same side of the mass. When this was

controlled, efforts were made to cut away as much of the material as was still at a dangerously high temperature. Charred straw and manure to a depth of about 2 feet throughout the greater part of the length of the pile were removed. The material was firmly packed, black, dry, and brittle to a depth considerably beyond any possible penetration by the fire. (Fig. 2.)

The temperatures of various points in the mass were determined with the aid of a thermocouple and a potentiometer. Holes were made by forcing a long iron rod into the pile; the thermocouple was inserted in the openings. A series of readings (Table 1) indicated that in the center of the pile and up to within 5 or 6 feet of the outer surface the temperatures were not extremely high, averaging only about 51° C.; 66° was the maximum. The temperatures of the outer layers, however, were considerably higher. In places where the manure was firmly packed, as on the dismantled side, the highest temperature was usually within 6 inches of the surface, whereas on the top, where recent additions still lay more or less loosely, the maximum temperature was usually found from 1½ to 2 feet within the mass.

The temperature of the opposite or east side of the pile was also excessively high, though no fire had yet appeared. This side was watched carefully. The following afternoon, September 10, fire broke out on this side, appearing first, as the others had, at from 5 to 10 feet above the ground.

When this had been put out an inspection of the stack revealed so many hot areas along the edge that the entire side was removed under frequent sprinkling with water. (Fig. 3.)

The mass was packed so firmly that progress was slow and fire broke out twice before the work was completed. In one of the hottest sections (fig. 3, A) a forkful of material was removed and spread out upon the ground. The straw was hot and steaming. About one minute later the steam had changed to smoke, which increased in density until after about three minutes the material glowed a fiery red. Exactly the same conditions appeared in the stack adjacent to the spot from which the material had been removed.

Temperature readings of the glowing coals and adjacent materials (though those of the former are probably only approximate) gave the following results:

Temperature of glowing straw removed from pile.....	°C. 167
Temperature of glowing material remaining in pile.....	132
Temperature in stack 3 inches from glowing coals.....	80

The fire smoldered a few minutes, then went out. It is significant that the temperature of material only a few inches from the glowing coals was not above 80° C. Moisture determinations showed that material in the stack adjacent to the point where the red glow had appeared contained only 3.7 per cent of water, whereas material 2 feet away, apparently just as badly scorched and brittle, contained 30.2 per cent. Material from the top of the stack, which was hot but showed no signs of scorching, contained 66 per cent moisture.

Figure 4 shows the contrast between material which has undergone excessive heating without firing and normal material from the surface of the pile. The charred material was very dry and brittle.

As the heating mass of material offered excellent opportunities for study, the following day further data were obtained. In general, the mass had cooled considerably, though a few areas were still hot.

Since "spontaneous" ignition has been known to take place apparently only as the result of rapid oxidation, it was assumed that further temperature rise would be produced in the manure pile on the introduction of air, or, preferably, pure oxygen. A brass tube and the thermocouple were introduced simultaneously into the center of an area having a temperature of 82.5° C. At 11.25 a. m. oxygen was introduced from a pressure tank, and changes in temperature were carefully noted. The temperature immediately began to rise rapidly and continued to increase for one-half hour; the rate of oxygen flow was occasionally increased. (Table 2.) At 12 m. the temperature had reached 100° C., an increase of 26.5° in 36 minutes. Further aeration resulted in a slow cooling to 107° at 1 p. m. As the heating material was inclosed within the mass, the estimation of the oxygen requirements was purely conjectural. Thus it is not surprising if the oxygen rate most favorable for heat production was not maintained and only limited heating allowed to take place.

TABLE 3[2].—Temperatures obtained by introducing oxygen into hot area of manure pile (2 feet beneath side surface)

Reading	Time	Temperature	Oxygen flow	Reading	Time	Temperature	Oxygen flow
		° C.				° C.	
1	11.24 a. m.	82.5	Began.	8	11.43 a. m.	105.0	Increased.
2	11.25 a. m.	84.0		9	11.45 a. m.	107.0	
3	11.30 a. m.	94.0	Increased.	10	11.50 a. m.	108.0	
4	11.34 a. m.	100.0		11	12.00 m.	109.0	
5	11.36 a. m.	103.0		12	12.15 p. m.	108.5	
6	11.38 a. m.	104.0		13	1.00 p. m.	107.0	
7	11.41 a. m.	105.0					

Figures 6 and 7 show the manure pile on the Department of Agriculture farm in which spontaneous ignition was observed by James, Bidwell, and McKinney.

Several significant facts are to be noted in connection with this fire. The first point is the confinement of the heated areas to sections of the manure pile not deeper than 12 inches below the surface, in other words, to those locations in which oxidation could most readily take place. The second point is the rapidity with which the tem-

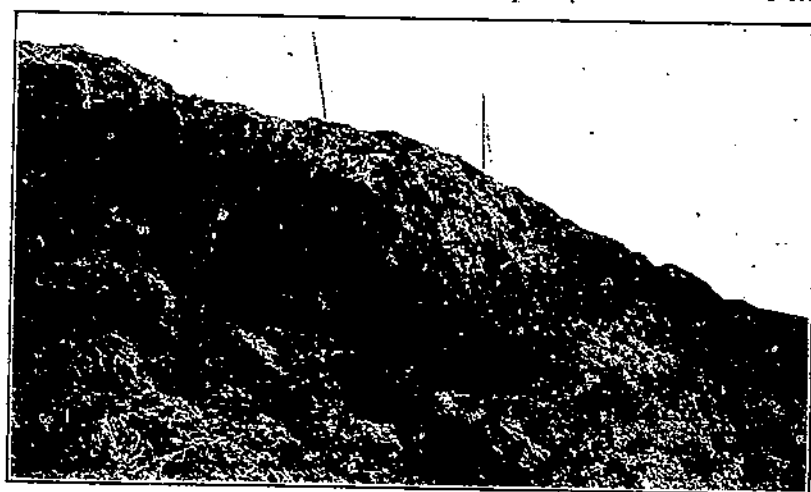


FIGURE 6.—Manure pile on the Department of Agriculture farm at Arlington, Va. Dark portion shows area where spontaneous ignition was observed in freshly withdrawn material

perature of material removed from the pile at 82° C. is raised to the state of ignition. The maximum temperature of 167° observed with the thermocouple in the glowing straw was undoubtedly far below the actual ignition degree because of the inadequate protection against radiation. There is here no opportunity for a previous production of pyrophoric carbon or iron (which requires temperatures of 250° to 300° for its formation) and unless we assume that pyrophoric materials can be produced at temperatures as low as 82° the only explanation apparently available for the sudden rise of temperature is the exceedingly rapid oxidation of highly unstable substances produced by anaerobic fermentations in the dense compact layers of the manure. The third point is the great variation

in moisture content between different parts of the manure pile, material adjacent to the point of ignition containing only 3.7 per cent water (a low percentage that was probably caused by the heat from the adjacent igniting mass), whereas material 2 feet away, apparently just as badly scorched and brittle, contained 30.2 per cent water, and litter on the top of the stack contained 66 per cent water. It was probably a lack of the exactly necessary conditions of moisture content that prevented the ignition of the manure when oxygen was introduced into a hot area of the pile having a temperature of 82.5°. The temperature could be raised only to 109°, when it began to diminish, the excess of easily oxidizable fermentation products having probably been destroyed.

Although the conditions existing in a pile of fermenting horse manure are different from those in hot haystacks, with a consequently different class of phenomena with respect to hot pockets and smoke



FIGURE 7.—Close-up view of manure pile shown in Figure 6 when heated material was being turned over and the fire quenched with water

channels, the basic causes of heat production and ignition are undoubtedly identical in both cases.

PRODUCTION OF COMPOUNDS OF HIGH CARBON CONTENT AT LOW TEMPERATURES

Miehe and others have raised an interesting question regarding the possibility of the production of pyrophoric carbon from hay at temperatures below 100° C. Experiments conducted by the author over a long period of years indicate that the reducing sugars of sugar-cane molasses may undergo even at ordinary temperature a slow spontaneous decomposition into products high in carbon and low in oxygen content as a result of the continued dehydroxylation of the sugars. These compounds, which are unsaturated, are of a colloidal character and with the progressive splitting off of hydroxyl groups become insoluble, approaching more and more the state of carbon but never attaining its actual composition. As the temperature of a hot haystack increases, the formation and decomposition of these humuslike products are undoubtedly accelerated and their affin-

ity for oxygen may possibly play some part in the final stages of heat production. It is doubtful, however, if a true carbon is ever produced from hay even at temperatures bordering upon the point of ignition.

Ranke commented upon the presence of empyreumatic substances in the hay carbon produced by heating hay to 250° C. in an oil bath and suggested that these volatile impurities, which were probably unsaturated, may have rendered his carbon pyrophoric, since after their destruction at higher temperatures the carbon no longer ignited spontaneously. Ranke in fact compared the possible spontaneous ignition of these impurities in hay carbon to that of oil upon waste. The difficulty of obtaining a pure carbon under such circumstances is indicated by the fact that even the purest vegetable carbons, obtained from sugar or cellulose, contain usually several per cent of hydrogen, which may be present in an absorbed gaseous state or in a resistant hydrocarbon combination. Laupper's results in rendering Ranke's hay carbon nonpyrophoric by treatment with acids may possibly have been produced by the removal or destruction of the retained easily oxidizable empyreumatic impurities and not from the solution of pyrophoric iron.

TEMPERATURE OF THE EXOTHERMIC REACTION OF HAY

The temperature of the exothermic reaction at which perfectly dry normal hay decomposes with evolution of heat is probably very close to that which Hawley (12) and other observers have found for wood, which is about 275° C., and this coincides with the temperature that Ranke and Laupper have set for the spontaneous ignition of hay as a result of pyrophoresis. If it is assumed that the temperature of hay can be raised to 275° as a result of the rapid spontaneous oxidation of unsaturated compounds, the sudden evolution of additional heat at the exothermic point will explain the ignition of the material without the necessity of assuming that this is due to the production of pyrophoric carbon or iron. Whether the temperature of the exothermic reaction for fermented hay is lower than that for normal hay (a factor of possible significance) remains to be determined.

LENGTH OF TIME NECESSARY FOR THE SPONTANEOUS IGNITION OF HAY

Miehe in the development of his theory of carbonization at low temperature calls attention to the fact that the period of heating at 70° C. may continue for several months. Although an interval of this extent has been observed in many cases of the spontaneous combustion of hay there are also well-authenticated instances where the period between the start of the bacterial heating of hay and the time of spontaneous ignition is only a few days. A case of this kind occurred on November 7, 1927, near Middlesex, Vt., during the heavy floods that devastated the valleys of the Winooski and other rivers of this section. (Fig. 8.) The scene of this fire was visited at the time by L. H. James and David J. Price (15) of the United States Department of Agriculture, from whose report the following observations are taken:

BARN FIRES IN VERMONT FLOODED AREAS

The unusual conditions in the Northern Vermont flooded areas, where the water reached the haymows of hundreds of barns, offered exceptional opportunities for studies relating to the spontaneous or self-heating of agricultural products. Observations were made by Department of Agriculture investigators in many barns in the Winooski, Lamoille, and Missisquoi River Valleys. Excessive heating set in almost immediately after the flood waters receded, in many cases endangering the houses and other farm buildings. The observations on spontaneous heating in Vermont barns can be summarized as follows:

1. The hay was covered with water ranging from one-half foot to 17 feet.
2. In every pile of wet hay observed some "heating" had taken place, many to the point of being considered dangerous.
3. Heat was generated in the bottom layers of the piles and, escaping up through the hay, led to the production of drafts of hot gases or "flues" that rose to the surface.
4. The large quantity of moisture carried with the hot gases from the lower layers was condensed on the upper, cooler hay, or in the air above. Many hay piles had been soaked throughout by the falling condensed moisture.*



FIGURE 8.—Destruction of a Vermont barn and silo by spontaneous ignition of hay following the flood in November, 1927

5. While the hot hay was being removed from the barns, one farmer observed charred materials.

6. The most marked evidence of excessive heating was observed by the farmers on the second and third days after the recession of the flood waters.

7. A clear-cut case of spontaneous ignition occurred near Middlesex, Vermont. This farm is in a narrow portion of the valley of the Winooski River where the flood waters rose exceptionally high. The barn contained about 50 tons of meadow hay and a little alfalfa. The hay had been kept in a bay in the rear of the barn and rested upon boards laid flat on the ground. The contents of the bay . . . consisted of:

- About 2 feet of the previous year's (1926) hay.
- About 6 inches of first cutting alfalfa (1927), which had rotted somewhat in the field but which was dried before being stored in the barn.
- About 45 feet of good meadow hay.
- About 6 inches of good, second cutting alfalfa (1927).
- About 6 inches of rowen on the top.

* Many farmers mentioned the strong odor of ammonia that was observed during the heating of the hay in the barns of the flooded areas of Vermont.

There was also a small pile of old dry straw on the barn floor.

The flood waters covered 17 feet of the pile of hay and most of the straw. No heating of the hay had been noticed before the flood, but considerable steaming was in evidence 24 hours after the waters had receded. The crest of the flood occurred early on Friday morning, November 4, 1927, and the barn burned between 4:00 and 5:00 p. m. on Monday, November 7, or about two days after the flood waters receded. On Sunday morning much heating had been noticed, and on Monday a distinctly charred odor was observed before the fire started. The barn burned to the ground and a silo, close by, fell over and was destroyed. It is interesting to note that the barn and hay stood in from three to five feet of water when the fire broke out.

The weather conditions at the time of the Vermont floods are indicated by the following quotations from the reports of the United States Weather Bureau for the station at Burlington, Vt.:

	November						
	1	2	3	4	5	6	7
Maximum temperature.....	61° F.	69° F.	43° F.	40° F.	48° F.	40° F.	36° F.
Rainfall (inches).....	0.00	0.52	3.75	1.35	Trace.	0.15	0.08

It will be noted that the maximum temperatures at the time of the Middlesex flood and fire were low. No evidence of spontaneous heating was noticed in the hay before the time of the flood. The interval between the time when the hay was first wet and spontaneous heating began and the time when the fire broke out was less than five days, a period that is much too short for the formation of pyrophoric carbon at low temperature as suggested by Miele.

UNSATURATED SUBSTANCES OCCURRING NATURALLY IN HAY

There remains finally to be considered the statement of Haldane and Makgill that the heat of oxidation of perfectly sterile hay in a sufficiently large pile will eventually lead to spontaneous ignition. The only unsaturated substances that occur naturally in hay are vegetable oils, which are too small in amount to be of significance, and the lignin, which constitutes about 25 per cent of the dry material of the hay. Lignin as it occurs naturally in hay and straw in association with cellulose and pentosans does not appear to be readily subject to spontaneous oxidation, although in the changes to which it may be subjected during the heating of hay there is a possibility of its being converted into some more easily oxidizable compound. The possibility of perfectly dry, well-cured hay ever absorbing enough oxygen from the air to ignite spontaneously, without the agency of fermentation, appears too remote to be of practical significance.

Flammable gases, pyrophoric substances, and some of the other factors enumerated by Laupper in his diagram of the spontaneous combustion process may possibly play a contributing part in the final stages of the phenomenon.

But these adjuncts of the process of spontaneous heating, in the author's opinion, are to be regarded more as effects than as causes of the primary reaction. The writer believes that future progress in the study of the problem of the spontaneous combustion of hay and of other agricultural products will be made chiefly in the careful

chemical investigation of the unstable unsaturated intermediary substances which are produced by microbial action and whose rapid oxidation leads to the high temperatures that result in final ignition.

NEED OF FUTURE INVESTIGATIONS

The determination of the exact conditions that produce the spontaneous ignition of hay, cattle feeds, horse manure, and other agricultural products is one of the most important problems in the field of agricultural research. As most truly pointed out by Professor Tschirch, of Switzerland, a prerequisite for preventing the enormous financial losses that occur each year from spontaneous combustion is exact definite knowledge as to how such fires are produced.

The answer to the problem can be obtained only by extensive cooperative experiments by chemists, bacteriologists, and engineers upon the changes that take place in large piles of fermenting hay. The piles must be sufficiently large (5 tons or more) to furnish the retention of heat and insulation that are necessary to produce spontaneous ignition of the hay.

In observing the changes that take place in large piles of fermenting hay and developing methods for the prevention of spontaneous heating and ignition, investigators must give special attention to the following factors:

The rate of heat production in different parts of the mass of material.

The changes in chemical composition of the hay.

The oxygen-consuming power of fresh and fermented hay and of extracts from the same.

The migration of moisture from the warmer to the cooler parts of the stack.

The production of gases in different parts of the pile.

The effect of the entrance of outside air at various stages of storage upon producing an increase of temperature in different parts of the pile.

A study of the conditions existing in the areas of highest heat production.

The effect of various methods of curing the hay.

The effect of the addition to the hay of salt and other substances.

The employment of ventilating flues and other devices.

The experiments must be conducted with the most improved apparatus for the automatic recording of temperatures in different parts of the hay pile, for the collection of gases, for the determination of moisture content, and for conducting the numerous bacteriological, analytical, and engineering investigations demanded by a research of this kind.

While such an investigation must extend over a period of several years and while the costs for material, apparatus, personnel, and other expenses for a large-scale cooperative research of this kind will be considerable, the expense, in view of the immense agricultural and industrial losses which result each year from spontaneous combustion, will be amply justified. It is only by such research that the exact causes of the spontaneous combustion of hay and other agricultural products can be determined and that satisfactory means for its prevention can be found.

LITERATURE CITED

- (1) BACON, SIR F.
1802. *NOVUM ORGANUM*. Translated by P. Shaw. 2 v. London.
- (2) BERTHELOT [M. C. P.]
1904. RECHERCHES SUR LES ÉCHANGES GAZEUX ENTRE L'ATMOSPHÈRE ET LES PLANTES SÉPARÉES DE LEURS RACINES ET MAINTENUES DANS L'OBSCURITÉ. *Compt. Rend. Acad. Sci. [Paris]* 138: 602-607.
- (3) BOEKHOUT, F. W. J., and VRIES, J. J. OTT DE.
1904-15. UEBER DIE SELBSTERHITZUNG DES HEUES. *Centbl. Bakt. [etc.]* (II) 12: 675-681, illus. (1904); 15: 568-573 (1905-06); 21: 398-407 (1908); 23: 106-108 (1909); 44: 290-304, illus. (1915).
- (4) BOERHAAVE, H.
1727. A NEW METHOD OF CHEMISTRY . . . Translated from the printed ed. by P. Shaw and E. Chambers . . . 3 pts., illus. London. [Pt. 1-2 and Pt. 3 separately paged.]
- (5) BROWNE, C. A.
1925. THE SPONTANEOUS DECOMPOSITION OF BUTTER FAT. *Indus. and Engin. Chem.* 17: 44-47, illus.
- (6) BURRI, R.
1919. DIE SELBSTERHITZUNG LAGERNDER PFLANZEN MASSEN MIT BESONDERER BERÜCKSICHTIGUNG VON HEU UND EMD. *Landw. Jahrb. Schweiz Jahrg.* 33:[23]-37.
- (7) COHN, F.
1891. UEBER WÄRME ERZEUGUNG DURCH SCHIMMELPILZE UND BAKTERIEN. *Jahresber. Schles. Gesell. [Breslau]* (1890) 68: 23-29.
- (8) COLUMELLA, L. J. M.
1773. DE RE RUSTICA. (*In Scriptores Rei Rusticæ Veteres Latini, Cato, Varro, Columella, Palladius . . . Ed. by M. Gesnerus. Ed. 2, Bk. 1, 938 p., illus. Lipsiae. 1773.*)
- (9) DESCARTES, R.
1644. *PRINCIPIA PHILOSOPHIAE*.
- (10) GÜPERT, H. R.
1830. UEBER DIE WÄRME-ENTWICKELUNG IN DEN PFLANZEN, DEREN GEFRIEREN UND DIE SCHUTZMITTEL GEGEN DASSELBE. 272 p. Breslau.
- (11) HALDANE, J. S., and MARGILL, R. H.
1923. SPONTANEOUS COMBUSTION OF HAY. *Fuel in Sci. and Pract.* 11: 380-387, illus.
- (12) HAWLEY, L. F., and WISE, L. E.
1926. THE CHEMISTRY OF WOOD. 334 p., illus. New York, The Chemical Catalog Co. Inc.
- (13) HILDEBRANDT, F.
1927. BEITRÄGE ZUR FRAGE DER SELBSTERWÄRMUNG DES HEUES. *Centbl. Bakt. [etc.]* (II) 71: 440-490, illus.
- (14) JAMES, L. H., BIDWELL, G. L., and MCKINNEY, R. S.
1928. AN OBSERVED CASE OF "SPONTANEOUS" IGNITION IN STABLE MANURE. *Jour. Agr. Research* 36: 481-485, illus.
- (15) — and PRICE, D. J.
1928. OBSERVATIONS ON HEATING HAY IN THE FLOODED REGIONS OF NORTHERN VERMONT. *Science (n. s.)* 67: 322-324, illus.
- (16) — RETTGER, L. F., and THOM, C.
1928. MICROBIAL THERMOGENESIS. II. HEAT PRODUCTION IN MOIST ORGANIC MATERIALS WITH SPECIAL REFERENCE TO THE PART PLAYED BY MICROORGANISMS. *Jour. Bact.* 15: 117-141.
- (17) LAUPPER, G.
1924. DIE NEUESTEN ERGEBNISSE DER HEUBRANDFORSCHUNG. *Landw. Jahrb. Schweiz Jahrg.* 34: [1]-54, illus.
- (18) —
1926. DIE SCHÄDEN DER LANDWIRTSCHAFT INFOLGE SELBSTENTZÜNDUNG DER HEUSTÖCKE. *Matér. l'Étude des Calamités Année* 3 (10): [112]-140, illus. [*In German. French summary p. 136-138, English summary p. 138-140.*]

- (19) LUCRETIVS, T.
1864. DE RERUM NATURA LIBRI SEX. Translated by H. A. J. Munro. 2 v.
London.
- (20) MEDEM.
1894. HEU-SELBSTENTZÜNDUNG UND DEREN VERHÜTUNG. Jahrb. Deut.
Landw. 9: 46-60, illus.
- (21) MIEHE, H.
1907. DIE SELBSTERHITZUNG DES HEUES. EINE BIOLOGISCHE STUDIE. 127 p.,
illus. Jena.
- (22) NELSON, E. K., and BROWNE, C. A.
1929. THE PROPERTIES AND CHEMICAL CONSTITUTION OF GLUCIC ACID. Jour.
Amer. Chem. Soc. 51: 830-836.
- (23) PLINY, G. (THE ELDER).
1892. NATURALIS HISTORIAE. Ed. by C. Mayhoff. v. 3, Libri 16-22, 496 p.
Lipsiae.
- (24) RANKE, H.
1873. EXPERIMENTELLER BEWEIS DER MÖGLICHKEIT DER SELBSTENTZÜNDUNG
DES HEUES (GRUMMETS). Ztschr. Landw. Ver. Bayern Jahrg. 63 (März
Heft): [87]-95. (Also published in Liebigs Ann. Chem. 167:
361-368. 1873.)
- (25) THOMPSON, N. J.
1928. THE SPONTANEOUS HEATING OF OILS. Oil & Fat Indus. 5: 317-326,
illus.
- (26) THUCYDIDES.
1876. HISTORY OF THE PELOPONNESIAN WAR. Translated by Bostick and
Riley. v. 1. London.
- (27) TSCHIRCH, A.
1918. DIE ENTZÜNDUNG DER HEUSTÖCKE. Mitt. Naturf. Gesell. Bern 1917:
[133]-137.
- (28) ——— and BARREN, A.
1924. UEBER DAS RANZIGWEIDEN DER FETTE. Schweiz Apoth. Ztg. 62:
281-285, 293-295, 404.
- (29) WALLACE, H.
1892. CLOVER CULTURE. 156 p., illus. Des Moines, Iowa.

ORGANIZATION OF THE UNITED STATES DEPARTMENT OF AGRICULTURE

September 11, 1929

<i>Secretary of Agriculture</i>	ARTHUR M. HYDE.
<i>Assistant Secretary</i>	R. W. DUNLAP.
<i>Director of Scientific Work</i>	A. F. WOODS.
<i>Director of Regulatory Work</i>	WALTER G. CAMPBELL.
<i>Director of Extension Work</i>	C. W. WARBURTON.
<i>Director of Personnel and Business Administration.</i>	W. W. STOCKBERGER.
<i>Director of Information</i>	M. S. EISENHOWER.
<i>Solicitor</i>	R. W. WILLIAMS.
<i>Weather Bureau</i>	CHARLES F. MARVIN, <i>Chief.</i>
<i>Bureau of Animal Industry</i>	JOHN R. MOHLER, <i>Chief.</i>
<i>Bureau of Dairy Industry</i>	O. E. REED, <i>Chief.</i>
<i>Bureau of Plant Industry</i>	WILLIAM A. TAYLOR, <i>Chief.</i>
<i>Forest Service</i>	R. Y. STUART, <i>Chief.</i>
<i>Bureau of Chemistry and Soils</i>	H. G. KNIGHT, <i>Chief.</i>
<i>Bureau of Entomology</i>	C. L. MARLATT, <i>Chief.</i>
<i>Bureau of Biological Survey</i>	PAUL G. REDINGTON, <i>Chief.</i>
<i>Bureau of Public Roads</i>	THOMAS H. MACDONALD, <i>Chief.</i>
<i>Bureau of Agricultural Economics</i>	NILS A. OLSEN, <i>Chief.</i>
<i>Bureau of Home Economics</i>	LOUISE STANLEY, <i>Chief.</i>
<i>Plant Quarantine and Control Administration</i>	C. L. MARLATT, <i>Chief.</i>
<i>Grain Futures Administration</i>	J. W. T. DUVEI, <i>Chief.</i>
<i>Food, Drug, and Insecticide Administration</i>	WALTER G. CAMPBELL, <i>Director of Regulatory Work, in Charge.</i>
<i>Office of Experiment Stations</i>	E. W. ALLEN, <i>Chief.</i>
<i>Office of Cooperative Extension Work</i>	C. B. SMITH, <i>Chief.</i>
<i>Library</i>	CLARIBEL R. BARNETT, <i>Librarian.</i>

This bulletin is a contribution from

<i>Bureau of Chemistry and Soils</i>	H. G. KNIGHT, <i>Chief.</i>
<i>Chemical and Technological Research</i>	C. A. BROWNE, <i>Chief.</i>
<i>Chemical Engineering Division</i>	DAVID J. PRICE, <i>Engineer in Charge.</i>

END