# STARCH

## ITS CHEMISTRY, TECHNOLOGY AND USES

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# STARCH

## ITS CHEMISTRY, TECHNOLOGY AND USES

A Handbook for the Student, the Analyst, the Consultant
and the Technologist concerned in the Manufacture and
Application of Starch and Starch Products

BY

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# PREFACE.

IT is now about forty-five years since a textbook dealing in a comprehensive manner with the chemistry and technology of starch has been published in the English language although several foreign works have appeared. During this period, our knowledge of the properties of starch has been enormously extended and our views concerning its constitution have been revolutionised whilst the technology of the manufacture of starch and starch products has been greatly developed both on the chemical and engineering sides.

In writing the present volume we have endeavoured to give a concise but fairly complete account of the chemistry of starch as it stands to-day, of the manufacture of starch and starch products in different countries, and of the uses to which starch and its products are applied. It is hoped that the book will prove useful to the student and to the technologist in starch manufacture and allied industries, and that it may serve as a work of reference to the chemist in general practice.

During the past decade, the problem of the constitution of starch has attracted the attention of a host of workers and great advances have been made towards its solution, although in the present state of our knowledge the reader will find it difficult to reconcile the various views concerning the nature of starch that have been put forward. It is probable, however, that with fuller knowledge the conflict between these views will prove more apparent than real.

We have endeavoured to give chapter and verse for statements which are beyond our personal experience, but in the description of the manufacture of potato starch we have availed ourselves of much information derived from O. Saare's excellent work *Die Fabrikation der Kartoffelstärke*, 1897, for which direct references are not given in the text. Our thanks too, are due to Messrs. Jahn & Co. of Arnswalde, and to Messrs. W H. Uhland, of Leipzig, for permission to reproduce the illustrations of up-to-date machinery and apparatus used in starch factories.

For aid in connection with the chapter on the Microscopy of Starch, we are indebted to Dr. E. Goulding, F.I.C., and Mr. S. J. Johnstone, B.Sc., F.I.C., of the Imperial Institute, who have kindly supplied us with numerous species and varieties of millet seed, and to Mr. T. E. Wallis, B.Sc., F.I.C., Lecturer in Botany to the Pharmaceutical Society, from whom we have obtained many of the starches of which photomicrographs have been made. These photomicrographs have been taken by Mr. T J. Ward to whom we must also express our thanks for the great pains he has taken and the excellent results he has obtained.

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# CHAPTER I.

## THE HISTORY OF STARCH.

THE preparation of starch from cereal grains has been known from very early times, having been described by Marcus Porcius Cato as far back as 184 B.C. According to Pliny the Elder,[1] the method of extracting starch from grain was discovered by the inhabitants of the Isle of Chios. Wheat appears to have been practically the only raw material utilised for the manufacture of starch from primitive times until the latter part of the eighteenth century.

In the Middle Ages the manufacture of wheat starch became an important industry in Holland and the Dutch obtained a high reputation for the quality of their starch. At that time and for long after starch found its principal use in the laundry for stiffening fabrics and it was regarded as an expensive luxury suitable for aristocrats, church dignitaries, etc. The custom of powdering the hair with starch appears to have originated in France in the sixteenth century, and towards the end of the eighteenth century the consumption of starch for this purpose alone was very considerable. It is interesting to note that Leonardo da Vinci, the pioneer of aviation, proposed to use starch to stiffen the fabric of the wings of flying machines.

Starch seems to have been introduced into England in the reign of Elizabeth, who is said to have appointed a special court official for laundry starching. In 1564, Mlle. van der Plane, a Flemish woman, came to London to establish a training centre for starching; she charged £5 a lesson and £1 for a récipé for making starch from wheat flour and other materials, from which it may be concluded that both the preparation and use of starch were regarded as household

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[1] *Historiæ naturalis.*

accomplishments in those days. Starch, however, was manufactured in England on an industrial scale at that time or soon afterwards, since in the reign of James I the industry attracted the attention of the State, being prohibited early in the reign on the ground that it involved the diversion of wheat from its more legitimate use as a food; shortly afterwards the industry was permitted to be carried on under supervision, prohibited again in 1610 and finally permitted again in 1622. It became customary to tint fabrics as well as to stiffen them, colouring matters being added to the starch for this purpose; various colours were employed, yellow being affected by men of fashion, green by Cavaliers and blue by Roundheads. In 1638, a Charter of Incorporation was granted by Charles I "for the remedying of many great abuses and inconveniences then complained of by the excessive and disorderly making of white starch in many places within this Realm by the converting and consuming great quantities of wheat and other grain fit for man's food into starch." In 1661 a new charter was granted by Charles II incorporating "sundry meet persons of the said trade of starch making with Power and Priviledges to them and to their successors to make or cause to be made, in one joint stock and not otherwise, in such convenient place or places as shall be appointed by Us . . . all and all manner of White Starch with Bran and Pollard only or with Wheat Corn or Grain imported from beyond the Seas or with musty, defective and unwholesome corn, unfit for the food of man, and not of any wholesome Corn or Grain of the Growth of this Realm . . ."

In the eighteenth century cheaper sources of starch than wheat were sought for. In 1732 the Sieur de Guife recommended to the French Government that potatoes should be used for the manufacture of starch, and in Germany the potato starch industry, fostered by Frederick the Great, dates from 1765. Duhamel du Monceau,[1] writing in 1772, observed that when cereals were dear recourse was made to other sources of starch such as arrowroot, potatoes, arum, etc. Du Monceau described the methods of manufacturing

[1] *Arts et Metiers*, 20.

starch in vogue at that time and mentioned that starch was employed by perfumers for making cosmetic powders, by dyers, presumably for colour printing, by cardboard manufacturers, by confectioners in making pastilles and by soap manufacturers as an ingredient of certain classes of soap. In 1796, Murray[1] patented a process for extracting starch from horse chestnuts and in 1797 Gibbs proposed to use the roots of *Arum maculatum* for starch manufacture.

The nineteenth century witnessed an enormous expansion of the starch industry, due largely to the demands of the textile, colour printing and paper industries and to the discoveries that starch is readily converted by suitable treatment into glucose and dextrin. From the beginning of the nineteenth century potatoes have been largely used for starch manufacture (chiefly in Germany), then followed maize which is the principal raw material in the United States, and from about 1850 rice also has been employed on the large scale.

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[1] E.P. 2096 of 1796.

# CHAPTER II.

## STARCH IN ITS RELATION TO PLANT METABOLISM.

In order to obtain a clear idea of the significance and importance of starch in relation to vegetable physiology, a brief account must first be given of the nature of plant structure and of the structural unit known as the cell.

Apart from a few exceptions, all plants consist of systems of cells. Some of the simpler fungi consist of a single cell but the vast majority of plants consist of more or less complex systems of cells. In some plants the cells are all of one kind but in most they are differentiated into groups according to the functions they perform. Cells vary greatly in size and shape; some are barely distinguishable even under fairly high magnification whilst others are easily seen with the naked eye and whereas some cells are more or less spherical or polyhedral, others are very narrow and elongated.

The cell itself consists of a mass of living matter, of protein character, called protoplasm surrounded by a closed membrane —the cell wall—which generally consists of cellulose. In the young cell, the protoplasm occupies the whole interior, but as the cell grows the protoplasm, which remains in contact with the cell wall over the whole interior surface of the latter, does not increase sufficiently in bulk to fill the cell completely so that cavities, known as vacuoles, are formed. A cell may contain a number of vacuoles; these increase in size as the cell grows and may coalesce to a single large vacuole. The vacuoles are filled with an aqueous solution of salts, sugars, etc., known as the cell sap which also permeates the whole cell. The protoplasm contains a nucleus and a number of bodies called plastids consisting of differentiated portions of the protoplasm. The plastids may be colourless or coloured. The colourless plastids are called leucoplastids or leucoplasts; those of a green colour (due to the green colouring matter chlorophyll) are called chloroplastids or chloroplasts, and those containing colouring matter other than chlorophyll are called chromoplastids or chromoplasts. The leucoplasts occur in parts of the plant which are not exposed to light and if, during the growth of a plant, any part previously in darkness becomes exposed to light, the leucoplasts which that part contains are converted into chloroplasts. The chloroplasts occur in the parts of the plant exposed to light, and it is to them, or rather to the chlorophyll they contain, that the green colour of plants, and especially of foliage leaves, is due. If a plant is kept in darkness it becomes colourless, the chloroplasts being converted into leucoplasts. The leucoplasts and chloroplasts serve to produce reserve and transitory starch in the plant and the mechanism of this intricate synthesis must now be considered.

An observation of great significance for the synthesis of complex organic compounds such as proteins, sugars and starch was made in 1783 by Senebier who found that the oxygen given off by green plants when exposed to sunlight is derived from the decomposition of carbon dioxide. Chlorophyll is essential to effect this decomposition so that plants which do not contain chloroplasts, the chlorophyll-bearing bodies, are incapable of utilising carbon dioxide. The function of the chlorophyll is to use the energy presented to it in the form of sunlight to effect this decomposition. The question naturally arises as to what, beside oxygen, is produced by this decomposition, and A. von Baeyer[1] suggested that formaldehyde is the first product, thus

$$\begin{array}{ccccccc} CO_2 & + & H_2O & = & HCOH & + & O_2 \\ \text{Carbon} & & \text{Water} & & \text{Formal-} & & \text{Oxygen} \\ \text{dioxide} & & & & \text{dehyde} & & \end{array}$$

the formaldehyde being polymerised to a sugar and the latter to starch. This view was borne out by the results of E. Fischer's work on the synthesis of sugars from formaldehyde and strikingly confirmed by T. Bokorny[2] who found that if the green alga, *Spirogyra*, is grown in an atmosphere free from carbon dioxide and in presence of disodium phosphate and the compound of formaldehyde

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[1] *Ber.*, 1870, **3**, 68.

[2] *Ber. Deut. bot. Ges.*, 1891, **9**, 103.

and acid sodium sulphite, starch is formed in abundance. Bokorny subsequently found[1] that *Spirogyra maxima*, under the influence of light, readily produces starch from sucrose, dextrose, glycerol, etc., in presence of oxygen. Further evidence that carbon dioxide is the raw material from which plants obtain carbon for the synthesis of starch was adduced by Pfeffer who observed that no starch is formed in the chloroplasts when plants are kept in an atmosphere free from carbon dioxide even though the plants are exposed to intense sunlight, and Pfeffer's observation was supplemented by Godlewski[2] who found that already-existing starch disappears from the chloroplasts under these conditions and that the formation of starch in the chloroplasts can be accelerated by increasing the proportion of carbon dioxide in the atmosphere around the plant.

The occurrence of starch granules in the chloroplasts was first observed in 1838 by H. von Mohl[3] and was subsequently investigated by J. Sachs[4] who found that the formation of starch in the chloroplasts depends on the same condition as the assimilation of carbon dioxide, viz. the presence of light. Sachs also found that if green plants are placed in darkness the starch soon disappears from the chloroplasts but re-appears on exposing the plant to light again. The great significance of these results will be obvious when it is remembered that alternate exposures to daylight and darkness constitute the normal state of plant life. During the day each green leaf produces starch in amount depending on the intensity of the light to which the leaf has been exposed. During the succeeding night this starch is dissolved in greater or less degree and transferred to other parts of the plant as required for growth, a fresh supply of starch being elaborated in the leaf on the following day. Both the solution and the accumulation of starch in the green parenchyma of leaves during the day are influenced by the intensity of the light and the temperature. Thus, V. Lubimenko[5] found that in latitudes north of 60° N.

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[1] *Chem. Zeit.*, 1896, **20**, 1005.

[2] *Flora*, 1873, **56**, 378.

[3] *Ann. Sci. Nat.*, 1838, [9], 150.

[4] *Bot. Zeit.*, 1862, **20**, 365; 1864, **22**, 289.

[5] *Compt. rend.*, 1926, **182**, 651,

the green parenchyma of the leaves is seldom wholly depleted of starch during the night, the leaf beginning to accumulate starch again on the succeeding day although it still retains some of the preceding day's store. South of latitude 50° N. the starch reserve in the leaves is often entirely depleted during the night. It is generally during the first half of the day that the amount of starch in the leaves attains its maximum; it then decreases and begins to increase again towards evening, and finally decreases to a minimum during the night. The course of accumulation and solution of the leaf starch varies, however, with different species of plants. Some (e.g. *Nicotiana tabacum*) show one maximum and one minimum daily; others (e.g., *Phaseolus vulgaris*) have two maxima and two minima whilst others (e.g. *Robinia pseudacacia*) are distinguished by several maxima and minima.

The periodic changes in the starch-content of foliage leaves can be easily demonstrated by the following method of Sachs[1]:—The fresh leaves are killed by immersion in boiling water for 10 minutes, then bleached by immersion in 96 per cent. alcohol at 50–60° C. for 15–30 minutes, and finally placed in a solution of iodine in potassium iodide solution for several hours. The leaves remain yellow or brownish yellow if there is no starch in the chloroplasts, they appear blackish if very little starch is present, dull black with a considerable amount of starch and black with metallic lustre if the leaves are very rich in starch.

A more delicate method is that of A. Meyer, improved by A. F. W. Schimper.[2] The leaf is first completely decolorised with alcohol and then immersed in a concentrated solution of chloral hydrate to which a small quantity of iodine has been added; the leaf tissue becomes very transparent and the swollen starch granules, stained with iodine, can be examined *in situ* under the microscope. The method is not so expeditious as that of Sachs, but it allows of the detection of very minute traces of starch, and owing to the fact that the leaf is not treated with boiling water, the exact distribution

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[1] *Arbeiten des Botanischen Instituts in Würzburg*, 1884, **3**, 1.

[2] *Bot. Zeit.*, 1885, **43**, 737.

of the starch granules in the various parts of the leaf tissue can be easily demonstrated.

Chlorophyll, the colouring matter of the chloroplast, exhibits certain characteristic absorption bands when examined spectroscopically, and M. C. Timiriazeff[1] found that if foliage leaves are exposed to the spectrum, only those rays which are absorbed by chlorophyll can cause the formation of starch within the chloroplast.

The starch formed under the influence of light in the chloroplasts of the foliage leaves or other green organs of the plant is sometimes called transitory starch since it is only formed during the day to be broken down to simpler substances and translocated to other parts of the plant. Certain parts of the plant, however, which are not exposed to light can form and accumulate starch. The starch formed in the unexposed parts of the plant, however, is not synthesised from carbon dioxide like the starch of foliage leaves, since both light and chlorophyll are requisite for this, but it is formed by the leucoplasts from the sugars brought from the green parts of the plant, and, being stored in the organs of reserve such as seeds, tubers, rhizomes, etc., is sometimes called reserve starch. Since both leucoplasts and chloroplasts produce starch, the name amyloplast is sometimes used to include both. The function of the leucoplasts was investigated by Schimper[2] and the close relation between them and the chloroplasts was proved by Meyer[3] who showed that the latter, like the leucoplasts, can form starch from sugars and some other substances. Thus, dextrose, laevulose and galactose can be converted into starch by leaf parenchyma but these sugars are not equally suitable for different plants; most of the leaves which can produce starch at all, form it readily from a 10 per cent. solution of laevulose, a relatively small number produce it from dextrose, and very few from galactose, and it seems to be a general rule that the sugars naturally present in the plant lend themselves most readily to starch-formation in the leaf. The fact that the chloroplasts, which under normal conditions of

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[1] *Compt. rend.*, 1890, **110**, 1346.

[2] *Bot. Zeit.*, 1880, **38**, 881.

[3] *Bot. Zeit.*, 1886, **44**, 81.

plant life assimilate the carbon of atmospheric carbon dioxide to form starch can also produce starch from certain sugars has great significance for the mechanism of the synthesis of starch by plants. As H. T. Brown and G. H. Morris have pointed out[1] there is no radical difference between the formation of starch in the chloroplasts of an actively assimilating plant and its formation in those same chloroplasts from a sugar solution. Though starch is the first visible product of assimilation there is little doubt that between the inorganic substances entering into the first chemical process of assimilation and the starch there is a whole series of substances of the sugar class and it is from the last members of this series that the chloroplasts, under normal conditions, elaborate their starch. Both under the natural conditions of assimilation and the artificial conditions of nutrition with sugar solutions the chloroplasts form their included starch from antecedent sugar.

The ratio between the amount of starch formed by the leaf and the amount of intermediate sugars, etc., formed in the course of assimilation appears to vary with the conditions. According to A. Meyer,[2] starch is only produced in the leaf when the amount of nutritive starch-forming material produced is greater than the leaf requires for its own growth and respiration. A similar view was held by A. Saposchnikoff[3] and the theory was put to the test of experiment by Brown and Morris[4] who found, for the leaves of *Helianthus annuus*, that whilst the total quantity of assimilation products amounted to 12 grms. per sq. metre per 12 hours of daylight, the increase of starch during this period was only 1·4 grms. or 8·6 per cent. of the total assimilation products. Brown and Morris concluded that "there is no evidence whatsoever of starch being a necessary link between the sugars of assimilation and the sugars of translocation; it is far more probable that starch is only elaborated within the cell when the supply of nutriment is in excess of the cell requirements and that most of the assimilated products never pass through the stage of starch at all."

[1] *Chem. Soc. Trans.*, 1893, **63**, 623.

[2] *Bot. Zeit.*, 1886, **44**, 81.

[3] *Ber. Deut. bot. Ges.*, 1890, **8**, 233.

[4] *Chem. Soc. Trans.*, 1893, **63**, 633.

With regard to the kind of sugar or sugars formed in the course of synthesis of starch in the leaf, diverse views have been held. Schimper[1] considered that dextrose is formed intermediately and that it is converted into starch when the quantity of sugar in the cell exceeds a certain maximum which varies in different plants. Brown and Morris[2] found that the leaves of *Tropaeolum majus* contain sucrose, dextrose, laevulose and maltose, the last-mentioned being, not an intermediate product of starch synthesis, but a product of subsequent starch degradation as will be seen later )see p. 13). From these and further experiments, Brown and Morris concluded[3] "that at any rate in the leaves of *Tropaeolum* cane sugar (sucrose) is the first sugar to be synthesised by the assimilatory process. There seems every reason to believe that this cane sugar, which may be regarded as the starting point of all the metabolic changes taking place in the leaf, functions, in the first place as a temporary reserve material and accumulates in the cell sap of the leaf parenchyma when the processes of assimilation are proceeding vigorously. When the degree of concentration of the cane sugar in the cell sap and protoplasm, exceeds a certain amount, which probably varies with the species of plant, starch commences to be elaborated by the chloroplasts, this starch forming a somewhat more stable and permanent reserve material than the cane sugar, a reserve to be drawn upon when the more easily metabolised cane sugar has been partially used up. That the starch formed by the chloroplasts is, strictly speaking, not autochthonous but owes its origin to antecedent cane sugar, is rendered probable not only from a consideration of the results we have described, but also from experiments upon the artificial nutrition of leaves by solutions of carbohydrates and from certain results which we described in 1890[4] on the starch-producing powers of some of the sugars when used as a nutrient for the cultivation of embryos of barley. In both these cases cane sugar was found to far surpass all

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[1] *Bot. Zeit.*, 1885, **43**, 738.
[2] *Chem. Soc. Trans.*, 1893, **63**, 666.
[3] *Loc. cit.*, 673.
[4] Brown and Morris, *Chem. Soc. Trans.*, 1890, **57**, 484.

other carbohydrates in bringing about the production of starch in the tissue of the leaf or young plant; so much so in fact as to suggest that under natural conditions of plant growth cane sugar is an antecedent of the formation of starch by the chloroplasts, a conclusion which, we think, is favoured by our more recent work." Brown and Morris also considered that that part of the sucrose in the leaf which is not converted into starch, is translocated, as required, to other parts of the plant in the form of dextrose and laevulose. Their view that sucrose represents an intermediate stage of the synthesis of starch in the leaf has been confirmed by W. A. Davis, A. J. Daish and G. C. Sawyer[1] in their investigation of the carbohydrates of the mangold leaf.

As has been stated already, the starch formed in the leaf during the day is, in greater or less degree, dissolved and translocated to other parts of the plant either to be utilised directly for growth or to be accumulated in the organs of reserve. This solution of starch which takes place in the leaf prior to translocation is not mere solution in the physical sense since such solutions of starch would be of colloidal nature and quite incapable of diffusing through the walls of the containing cells; the solution of starch in the leaf involves hydrolysis to a simpler substance or substances capable of diffusion through the cell walls. We have now to consider the means whereby this hydrolysis is effected and the nature of the hydrolytic products.

The existence of an enzyme in seeds of the graminae, capable of liquefying and saccharifying starch was discovered as long ago as 1833 by Biot and Persoz,[2] but a systematic investigation on the occurrence of this enzyme—diastase—in various plant tissues appears first to have been made in 1878 by Baranetzky[3] who found, amongst other results, that some stalks and foliage leaves exhibit considerable diastatic power. L. Brasse[4] examined the foliage leaves of a number of plants, viz., potato, dahlia, Jerusalem artichoke, maize,

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[1] J. *Agric. Sci.*, 1916, **7**, 255.

[2] *Ann. Chim. Phys.*, 1833, **52**, 72.

[3] Die stärke umbildenden Fermente in den Pflanzen, Leipzig, 1878.

[4] *Compt. rend.*, 1884, **99**, 878.

beetroot, tobacco and rice, and found diastase in all. J. Wortmann[1] on the other hand considered that foliage leaves contain little or no diastase and that dissolution of starch in the leaf is effected directly by the protoplasm. The view that diastase is responsible for the solution of leaf starch was supported by S. H. Vines[2] and was finally proved beyond question by Brown and Morris[3] who examined a large number of foliage leaves of different plants and found not only that all contain diastase but that many contain sufficient to hydrolyse, under favourable conditions, many times more starch than the total dry weight of the leaf itself. Brown and Morris pointed out that it is only by drying the leaf that the full activity of the leaf diastase can be appreciated and they used the following method for determining the diastatic activity:—0·5 grm. of the finely powdered air-dried leaf is digested at 30° C. with 50 c.c. of a 2 per cent. solution of Lintner's soluble starch (see p. 54) for 48 hours, a blank with a boiled mixture of leaf and starch solution being made at the same time. The reducing power of the solution is determined as maltose (see Ch. XIII). If the degree of reduction exceeds Kjeldahl's proportionality law the determination must be repeated with a smaller quantity of leaf. Of the numerous species of leaves examined by Brown and Morris the following are quoted as showing the range of diastatic activity encountered:—

TABLE I.

| 10 grms. of air-dried foliage leaves. | Wt. of maltose produced in 48 hours at 30° C. |
|---|---|
| Pisum sativum (Pea) | 240·3 grms. |
| Phaseolus multiflorus (Scarlet runner) | 110·5 ,, |
| Lathyrus odoratus | 100·4 ,, |
| Lathyrus prætense | 34·8 ,, |
| Trifolium prætense (Red clover) | 89·7 ,, |
| Tropæolus majus | 3·7 to 8·3 ,, |
| Hydrocharis morsus-ranæ (Frog's bit) | 0·27 ,, |

The most active of the leaves examined, viz., that of *Pisum sativum*, was found to have a diastatic power equal to nearly

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[1] *Bot. Zeit.*, 1890, **48**, 582.

[2] *Ann. Bot.*, 1891, **5**, 409.

[3] *Chem. Soc. Trans.*, 1893, **63**, 604.

40 per cent. of that of an average pale malt. The *Leguminosae* are conspicuous for their high diastatic power with the exception of the lupin and the leaves of this plant are rich in tannin, a substance which as Brown and Morris found, tends to prevent the diastase from dissolving. The results with *Tropæolus majus*, quoted in the above table, show that the diastatic power may vary considerably in leaves of the same plant. With the exception of *Hydrocharis* (which contains much tannin), all the leaves examined contain far more diastase than would suffice to convert, within a moderate period of time, all the starch that the leaf could ever contain. From further experiments Brown and Morris concluded that the amount of diastase in the leaves of plants grown under natural conditions is subject to periodic fluctuations, and that the conditions which best promote assimilation and elaboration of starch in the leaf are those which militate against the accumulation of diastase, which occurs chiefly when the leaf is being depleted of starch and other products of assimilation. Brown and Morris were inclined to regard the increase in the amount of diastase in the leaf as a starvation phenomenon. Thus when daylight fails and assimilation of carbon dioxide falls off, the cells of the leaf soon use or translocate the excess of the soluble assimilable products, e.g. sucrose, and then draw on their reserve of starch, and to facilitate this the somewhat starved protoplasm now begins to elaborate diastase more rapidly.

With regard to the nature of the sugar formed from the starch, the existence of maltose in leaves at certain periods was demonstrated by Brown and Morris,[1] an observation affording further evidence that the dissolution of starch in the leaf is chiefly effected by diastase. More recently, however, Davis and Sawyer[2] from a study of the carbohydrate metabolism in the potato leaf, concluded that the starch appears to be converted directly into glucose and suggested that the degradation of starch in the leaf is effected by a mixture of enzymes in which maltase predominates.

Fungi, unlike higher, chlorophyll-containing plants, cannot

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[1] *Chem. Soc. Trans.*, 1893, **63**, 635.

[2] *J. Agric. Sci.*, 1916, **7**, 352.

assimilate carbon dioxide, but it has been found that some of them resemble the higher plants in possessing the power of synthesising starch from sugars and certain other organic compounds. Thus, F. Boas[1] found that if the well-known mould, *Aspergillus niger*, is grown in a solution of glucose, laevulose, sucrose or dextrin containing ammonium nitrate as source of nitrogen together with small quantities of magnesium sulphate and secondary potassium phosphate, at a temperature of about 33° C., a substance is obtained, both in the solution, from which it is precipitable by alcohol, and attached to the cell-walls of the mould, which gives the reactions of starch. The same substance is formed when beer wort, containing, besides maltose and dextrin, small quantities of dextrose and laevulose, and acidified with small quantities of sulphuric or phosphoric acid or with considerable quantities of tartaric acid, is used as nutrient medium. The presence of free acid appears to be essential to the production of the starch-like substance; when ammonium nitrate is used as source of nitrogen, its decomposition supplies the requisite acidity.

E. C. Grey[2] found that if a culture of *Bacillus coli* is grown anaerobically at 37° C. in a solution of glucose containing nitrogenous and mineral nutriment, starch is formed fairly abundantly. Thus, Grey found a quantity of starch corresponding to 9 per cent. of the amount of glucose fermented, the total amount formed being probably much greater, since the amount found only represents the excess of what is formed over what is decomposed. The starch formed is rapidly hydrolysed by the bacterial enzymes.

With regard to the distribution of starch in the various organs of the higher plants it may be observed that although very large quantities of starch are elaborated in the foliage leaves the amount of starch actually present in the leaves at any one time, even at the end of a sunny day, is comparatively small, each day's accumulation being more or less completely dissolved and removed. It is only in the reserve organs of the plant that starch is accumulated in such quantities as to

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[1] *Biochem. Zeitsch.*, 1917, **78**, 308; **81**, 80.

[2] *Biochem. J.*, 1924, **18**, 712.

pay for extraction on the industrial scale, e.g. in the tubers of the potato (*Solanum tuberosum*), the roots of the cassava (*Manihot utilissima*) and yam (*Dioscorea*), the rhizomes of *Maranta arundinacea* and *Curcuma longa*, and the seeds of various cereals. Further, whereas the starch of the reserve organs is generally characterised by the comparatively large size of the granules, the starch of other parts of the plant such as the leaf consists of very small granules and would therefore be difficult to extract.

According to Schimper[1] and Meyer,[2] starch granules in the plastids grow, chiefly if not entirely, by apposition, and the laminated or stratified structure of the granules which is so strikingly exhibited by many starches under the microscope, is the result of the growth of the granules by the apposition of successive layers. Since the plant may need to draw on its starch reserve on occasion, it is obvious that the granules may have periods of solution alternating with periods of growth. The shape of the starch granules, which varies, not only from plant to plant, but also in different organs of the same plant, depends on the conditions under which the granules are formed; thus, seed tissues which store their starch slowly and without interruption, form more or less spherical granules with their layers or strata centrically disposed; granules that develop under less uniform conditions are likely to be less regular in shape; the excentric stratification observed with many starches appears to be due to contact between granule and plastid being restricted to one side of the granule, growth then being limited to that side only.

The plastids may form single starch granules or they may form a few or many granules which grow together in aggregates known as compound granules and occasionally the latter become enveloped in one or more layers of starchy substance common to the whole aggregate. Compound granules which are thus enveloped are known as semi-compound granules.

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[1] *Bot. Zeit.*, 1881, **39**, 185.

[2] *Untersuchungen über die Stärkekörner, Jena*, 1895.

# CHAPTER III.

## THE CONSTITUTION OF STARCH.

*Quot homines tot sententiae.*

In the year 1811 it was observed by Vauquelin[1] that starch is converted into a gum-like, soluble substance when heated somewhat strongly, and at about the same time Kirchoff[2] made the important discovery that starch yields a crystallisable sugar when boiled with dilute sulphuric acid, and subsequently found[3] that it also yields sugar when subjected to the action of grain. In 1812 Vogel[4] found that in addition to a sugar a gum-like substance is formed when starch is treated with hot dilute acid. In 1833, this gum was further examined by Biot and Persoz[5] who gave it the name dextrin and these chemists pointed out that the action of malted grain on starch is due to a special agent to which they assigned the name "diastase." A valuable contribution to the study of the constitution of starch was made by Musculus[6] in 1860. This worker showed, contrary to the views previously held, that in the action of sulphuric acid or of diastase on starch, the sugar and dextrin are produced simultaneously by fission of the starch molecule accompanied by hydrolysis.

The most characteristic product of the action of diastase on starch is the well-known sugar, maltose, but although this compound had been isolated by de Saussure[7] in 1819 and subsequently by Dubrunfaut, its existence was afterwards overlooked or forgotten, and for many years it was supposed

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[1] *Bull. Pharm.*, 1811, **3**, 54.
[2] *Schweigg. J.*, 1812, **4**, 108.
[3] *Ibid.*, 1815, **14**, 389.
[4] *Ibid.*, 1812, **5**, 80.
[5] *Ann. Chim. Phys.*, 1833, **52**, 72.
[6] *Ibid.*, 1860, **60**, 203; *Compt. rend.*, 1862, **54**, 194.
[7] *Ibid.*, 1819, **11**, 379.

that the sugar formed by the action of diastase on starch was dextrose, an erroneous view which caused much confusion in the interpretation of the results of the diastatic hydrolysis of starch. The subject was finally settled by C. O'Sullivan[1] who showed that maltose and dextrin are the sole products obtained when starch is dissolved by malt extract He also showed that the proportion of maltose to dextrin in the product of diastatic starch conversion decreases as the temperature at which conversion is effected is increased above 63° C. and expressed the view that the dextrins produced at different temperatures are identical. This view, however, he subsequently abandoned[2] and came to the conclusion that the nature of the dextrin varies according to the temperature at which the diastatic hydrolysis is carried out.

The existence of a number of dextrins derived from starch had been maintained by various chemists for some years prior to O'Sullivan's work. For the dextrin giving a red or brown colour with iodine, Brucke, in 1872, proposed the name "erythrodextrin" the dextrin giving no colour with iodine being designated "achroodextrin." In 1874 Naegeli found that if ungelatinised starch is subjected to the prolonged action of dilute mineral acid in the cold, it yields, after passing through the stage of soluble starch, a dextrin to which he gave the name "amylodextrin." In 1879 Herzfeld[3] subjected starch to the action of diastase restricted by heat and obtained a dextrin which he called "maltodextrin."

In the course of the next decade much light was thrown on the mechanism of the diastatic saccharification of starch and on the composition of the starch molecule by the painstaking work of H. T. Brown, J. Heron and G. H. Morris. In 1879[4] Brown and Heron found if malt extract is allowed to act at the ordinary temperature on starch paste, the latter undergoes rapid decomposition with the formation of maltose and dextrin in the proportion of 80·9 parts of the former to 19·1 parts of the latter. The same change occurs at all temperatures

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[1] *Chem. Soc. Trans.*, 1872, **25**, 579; 1876, **1**, 478; 1876, **2**, 125.

[2] *Ibid.*, 1879, **35**, 770.

[3] *Ber.*, 1879, **12**, 2120.

[4] *Chem. Soc. Trans.*, 1879, **35**, 596.

up to about 60° C., but if the malt extract has been previously heated to 66° C. or above, decomposition does not proceed so far, the saccharification product containing less maltose and more dextrin; if the product so obtained is then treated with unheated malt extract at 50–60° C. the mixture rapidly attains the composition corresponding to 80·9 parts of maltose and 19·1 parts of dextrin. The residual dextrin of the diastatic conversion of starch at temperatures below 60° C., is susceptible to a slow further decomposition by malt extract, but the rate of this decomposition is extremely slow by comparison with the preceding one. Brown and Heron concluded from these results, that in the saccharification of starch by malt extract at temperatures not exceeding about 60° C., a definite molecular decomposition of starch occurs corresponding to the above-stated proportions of maltose and dextrin; they suggested that the simplest formula for soluble starch is $10C_{12}H_{20}O_{10}$, and that, when subjected to the action of malt extract, the starch molecule successively loses single $C_{12}H_{20}O_{10}$ groups by hydrolysis to maltose, the residual part of the molecule at the successive stages representing a succession of dextrins of decreasing complexity. The removal of eight such groups corresponds to the condition attained in saccharification with malt extract below 60° C. and may be represented by the equation:—

$$\begin{array}{ccccccc} 10C_{12}H_{20}O_{10} & + & 8H_2O & = & 8C_{12}H_{22}O_{11} & + & 2C_{12}H_{20}O_{10} \\ \text{Starch.} & & \text{Water.} & & \text{Maltose.} & & \text{Stable Dextrin.} \end{array}$$

which, since it represents the eighth stage, or rather the sum of the first eight stages in the transformation, became known as the "No. 8" equation. This equation represents the definite stage in the diastatic hydrolysis of starch corresponding to a proportion of 80·9 parts of maltose to 19·1 parts of dextrin, noted above.

The nature of the intermediate dextrins formed in the hydrolysis of starch was subsequently investigated by Brown and Morris.[1] Naegeli had observed in 1874 that by the long continued action of dilute mineral acid on ungelatinised starch

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[1] *Chem. Soc. Trans.*, 1885, **47**, 527; 1889, **55**, 449, 462.

in the cold, a dextrinous substance is formed to which he gave the name "amylodextrin"; this substance is quite different from the soluble starch formed in the first instance, the latter, but not the former retaining the form of the starch granules. Brown and Morris investigated Naegeli's amylodextrin and concluded that it is a definite chemical compound of the formula

$$\left\{ \begin{matrix} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_6 \end{matrix} \right\};$$

it is completely hydrolysed to maltose by diastase without any pause in the reaction, and hence it cannot contain the stable amylin nucleus which forms one-fifth of the molecule of soluble starch and yields the stable dextrin produced in the unrestricted diastatic hydrolysis of starch. Brown and Morris also obtained another dextrin, to which they gave the name of "maltodextrin," by acting on soluble starch with malt extract previously heated above 65° C.; maltodextrin, which was found to have the formula

$$\left\{ \begin{matrix} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{matrix} \right\},$$

is, like amylodextrin, completely converted into maltose by unrestricted malt extract. An exhaustive study of maltodextrin was subsequently made by H. T. Brown and J. H. Millar[1] who found that it has a specific rotatory power of $[\alpha]_D = 181–183$ and a reducing power equal to 42–43 per cent. of that of maltose. Brown and Millar[2] also examined the stable dextrin formed by the action of unrestricted diastase on starch (see the "No. 8" equation, p. 18). This dextrin was found to have a specific rotatory power of $[\alpha]_D = 197–198°$ and a reducing power equal to 5·5 per cent. of that of maltose. From a study of the dextrinic acid obtained by oxidising the dextrin, and of the products of acid hydrolysis of the dextrinic acid, it was concluded that the stable dextrin of the "No. 8" equation has the formula

$$\left\{ \begin{matrix} C_6H_{12}O_6 \\ (C_6H_{10}O_5)_{39} \end{matrix} \right\},$$

[1] *Chem. Soc. Trans.*, 1899, **75**, 286.

[2] *Ibid.*, 315.

which corresponds to a molecular weight of 6498. The proportion of dextrin to maltose found in the product of hydrolysis of starch by unrestricted diastase when the definite resting stage is reached (represented by the "No. 8" equation) indicates that the magnitude of the molecule of starch cannot be less than five times that of stable dextrin. Hence starch must have a molecular weight of not less than 32400, its formula being represented by $100C_{12}H_{20}O_{10}$. If the formula is written thus:—

$$80C_{12}.H_{20}O_{10}.40C_{6}H._{10}O_{5}.$$

expression is given to the fact that that part of the molecule which yields stable dextrin on hydrolysis, differs from the remainder which directly and rapidly yields maltose under the influence of diastase; or the constitution of starch may be described as made up of the residues of 80 maltan groups, $C_{12}H_{20}O_{10}$ and 40 dextran groups $C_{6}H_{10}O_{5}$ probably linked in ring form by oxygen atoms; on diastatic hydrolysis, the dextran complex is split off with the formation of stable dextrin whilst the maltan portion of the ring is attacked at the oxygen linkings of the $C_{12}H_{20}O_{10}$ groups.

The views of Brown and his fellow-workers did not long remain unchallenged. In 1891, C. J. Lintner[1] claimed to have separated from a beer residue, a sugar identical with the isomaltose previously obtained by E. Fischer[2] by the action of cold, concentrated hydrochloric acid on glucose. The preparation of isomaltose by the action of diastase on starch was subsequently described by Lintner and Düll.[3] Although isomaltose itself was not obtained in a crystalline condition it was found to yield a well-crystallised osazone possessing the same properties as Fischer's isomaltosazone. As the result of further investigation dealing with the hydrolysis of starch by oxalic acid and by diastase, Lintner and Düll[4]

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[1] *Zeitsch. ges. Brauw.*, 1891, **14**, 281.
[2] *Ber.*, 1890, **23**, 3687.
[3] *Zeitsch. ges. Brauw.*, 1892, **15**, 6; *Zeitsch. angew. Chem.*, 1892, 263.
[4] *Ber.*, 1893, **26**, 2533; *Zeitsch. ges. Brauw*, 1894, **17**, 339; *Ber.*, 1895, **28**, 1522; *Chem. Zeit.*, 1897, **21**, 737.

concluded that the course of hydrolysis in the two cases is as follows:—

| Hydrolysis with Oxalic Acid. | Hydrolysis with Diastase. |
|---|---|
| Soluble starch. | Soluble starch. |
| Erythrodextrin I. | Erythrodextrin I. |
| Erythrodextrin II α. | — |
| Erythrodextrin II β. | — |
| Achroodextrin I. | Achroodextrin I. |
| Achroodextrin II. | Achroodextrin II. |
| Isomaltose. | Isomaltose. |
| Dextrose. | Maltose. |

According to these schemes the final products of the action of oxalic acid on starch are isomaltose and glucose, whilst that of the action of diastase is maltose. The isomaltose prepared by acid hydrolysis was found to be quite unaltered by diastase whereas that obtained in the course of diastatic hydrolysis was partly converted by diastase into maltose from which it would appear that the acid isomaltose and the diastatic isomaltose are stereoisomeric.[1]

The conflicting views concerning the course of the diastatic hydrolysis of starch as presented, on the one hand by Brown and his co-workers, and on the other by Lintner and Düll became the subject of controversy amongst numerous workers. The views of Lintner and Düll were supported by A. Schifferer[2] who concluded that the sole products of the action of diastase on starch are dextrin (or dextrins), isomaltose and maltose. H. Ost,[3] on the other hand, considered Lintner's isomaltose to be impure maltose and C. Ulrich[4] arrived at the same conclusion. A. R. Ling and J. L. Baker[5] considered that Lintner's isomaltose is not homogeneous, consisting partly of maltose and partly of a substance which may be a simple dextrin of the formula $C_{12}H_{20}O_{10}+H_2O$. Brown and Morris[6] pointed out that Lintner's case for the identity of his isomaltose with that obtained by Fischer by the action of cold hydrochloric acid on glucose appeared to rest solely on the similarity of

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[1] *Zeitsch. ges. Brauw.*, 1894, **17**, 378.
[2] *Neue Zeitsch. Rüb-Zuck. Ind.*, 1892, **29**, 167.
[3] *Chem. Zeit.*, 1895, **19**, 1501.
[4] *Ibid.*, 1895, **19**, 1523.
[5] *Chem. Soc. Trans.*, 1895, **67**, 702.
[6] *Ibid.*, 1895, **67**, 709.

crystalline habit and melting point of the osazones. The crystalline appearance and melting point of maltosazone are very greatly affected by small quantities of impurity, and after exhaustive experiments Brown and Morris concluded that Lintner's isomaltose is not a chemical entity but consists of a mixture of maltose and dextrinous compounds. E. Prior[1] also, regarded Lintner's isomaltose as a mixture of achroodextrins and maltose, and considered that the end-product of the diastatic hydrolysis of starch consists of:—

Achroodextrin I.
Achroodextrin II.
Achroodextrin III.
Maltose.

Of the three achroodextrins, No. III immediately precedes maltose in a starch conversion and is the difficultly fermentable constituent of wort. Ling and Baker[2] found that by the action of diastase on starch at 70° C., maltose and the following unfermentable substances are formed:—maltodextrin $\alpha$, identical with Brown and Morris's maltodextrin; maltodextrin $\beta$, identical with Prior's achroodextrin III, and a substance, $C_{12}H_{22}O_{11}$, isomeric with maltose, which may consist of the simple dextrin $C_{12}H_{20}O_{10} + H_2O$. By employing the diastase of ungerminated barley, Baker[3] found that the hydrolysis of starch follows a somewhat different course, only maltose and a dextrin being formed in the first hour or two although some glucose is subsequently formed from the dextrin; this dextrin, in consideration of its general behaviour and close relationship to the parent substance, starch, was called $\alpha$-amylodextrin by Baker although it differs markedly from the amylodextrin described by Naegeli and further investigated by Brown and Morris (see p. 19) The question of the existence of isomaltose was again raised in 1902 by V. Syniewski[4] who claimed to have isolated it in the pure state from the products of the diastatic hydrolysis of starch and proposed that it should be renamed "dextrinose." It should be mentioned here

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[1] *Bayerisches Brauer J.*, 1896, **6**, 385.

[2] *Chem. Soc. Trans.*, 1897, **71**, 508.

[3] *Ibid.*, 1902, **81**, 1177.

[4] *Annalen*, 1902, **324**, 212.

that A. Croft Hill,[1] by the action of maltase on glucose, obtained a disaccharide which he termed "revertose" but which was regarded by O. Emmerling[2] and by E. F. Armstrong[3] as isomaltose identical with the compound obtained by the action of cold hydrochloric acid on glucose. A. Georg and A. Pictet[4] have examined and compared Fischer's isomaltose (formed by action of hydrochloric acid on glucose), Lintner's isomaltose (formed by action of diastase on starch) and Croft Hill's revertose and conclude that these are three distinct substances, and they propose to retain the name "isomaltose" for Fischer's compound, to call Lintner's compound "dextrinose" as proposed by Syniewski and to call Croft Hill's compound "revertose" as proposed by him.

Of the various schemes for the mechanism of the diastatic degradation of starch that we have considered in the foregoing pages none takes account of glucose as a possible product of hydrolysis although it should be mentioned here that Brown and Millar[5] found that the stable dextrin of the "No. 8" equation is slowly and partially converted into a mixture of about equal parts of maltose and dextrose by diastase. In 1902 Ling and Davis[6] observed that if starch paste is saccharified with a solution of diastase that has been previously heated to 65–70° C., glucose is found among the final products of the reaction although this sugar cannot be detected in the product of the action of unrestricted diastase on starch; the maximum proportion of glucose is obtained with diastase that has been pre-heated in solution at 68–70° C. for 15–30 minutes, but does not exceed about 12 per cent. of the total hydrolytic products. Ling suggested that the reason that no glucose is found amongst the products of the action of unrestricted diastase on starch is that this sugar is immediately condensed by the action of the enzyme forming the isomaltose of Lintner (or the simple dextrin of Ling and Baker, see p. 21,

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[1] *Chem. Soc. Trans.*, 1903, **83**, 578.
[2] *Ber.*, 1901, **34**, 600, 2206, 3810.
[3] *Proc. Roy. Soc.*, 1905, **76B**, 592.
[4] *Helv. Chim. Acta.*, 1926, **9**, 612.
[5] *Chem. Soc. Trans.*, 1899, **75**, 315.
[6] *J. Inst. Brew.*, 1902, **8**, 475; *British Association Report*, 1903.

or the dextrinose of Syniewski, see p. 22); if, however, the diastase is pre-heated, its condensing action is weakened and the glucose formed can be isolated.

In 1903, L. Maquenne[1] observed that if starch paste is allowed to stand for some days under aseptic conditions, it gradually becomes opaque and finally deposits; the same phenomenon occurs in the case of the pseudo solution of starch obtained by heating starch with water under pressure to 130–150° C. This process, to which the name of starch reversion was given, is slow under ordinary conditions, but it is accelerated by addition of acid and to a remarkable degree by the enzyme, amylocoagulase, discovered by J. Wolff and A. Fernbach[2] in cereal grains and other parts of plants. Maquenne[3] found that the rate of reversion increases with the concentration of the starch paste and came to the conclusion that the precipitate of reverted starch, or amylose as it was subsequently termed, is not a single substance but a mixture of several different products of condensation. As the result of further work, Maquenne and E. Roux[4] came to the important conclusion that natural starch is a mixture of two substances of which one—amylose—is slowly precipitated from ordinary starch paste or from the solution obtained by heating starch with water under pressure, whilst the other, to which the name amylopectin was given, is the constituent to which the gelatinisation of natural starch is due. The amylose obtained by allowing starch paste to stand, gives no colour, in the solid state, with iodine, is not readily attacked by diastase, and is scarcely soluble in water even at 120° C.; if, however, it is heated with water under pressure at 150° C., it dissolves fairly readily to a clear solution which may be easily filtered. This solution gives a fine blue colour with iodine and is completely converted into maltose by malt extract at 56° C. On cooling an aqueous solution of amylose, the latter is thrown down as a white precipitate which is

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[1] *Compt. rend.*, 1903, **137**, 88, 797, 1266.
[2] *Ibid.*, 1903, **137**, 718; 1904, **138**, 819; 1904, **139**, 1217.
[3] *Ibid.*, 1904, **138**, 213, 375.
[4] *Ibid.*, 1905, **140**, 1303.

similar in appearance to the natural starches. E. Roux[1] prepared amyloses from different natural starches, by repeated solution in water at 155° C., and found that they all had similar properties. Although pure amylose requires to be heated with water to about 150° C. to effect solution, the amylose present in natural starch is completely soluble in boiling water; artificial amylose appears to be a mixture of highly condensed and only slightly soluble amyloses whereas the amyloses of natural starch are accompanied by lower homologues which act as solvents forming a kind of solid solution. The existence of the second constituent of starch —amylopectin—was inferred from the fact that starch, unlike pure amylose, forms a mucilaginous or viscous paste with boiling water and since this property is common to the various starches, the starches in general appear to contain amylopectin as well as amylose. Whereas the latter constituent is rapidly and completely converted into maltose by diastase, it was at first thought that amylopectin is liquefied only and not saccharified by diastase, and that, corresponding to the proportions of maltose and dextrin obtained in an ordinary diastatic starch conversion, starch contains about 80–85 per cent. of amylose and 15–20 per cent. of amylopectin. Natural starches, as well as malt extract, however, possess reactions somewhat on the alkaline side of the optimum point for diastatic action, and Maquenne and Roux[2] found that if the reaction is adjusted to the optimum point the saccharification of the starch is much more rapid and a larger proportion of maltose is obtained. Maquenne and Roux[3] concluded that amylopectin, like its amylose congener, is transformed into maltose by the prolonged action of malt extract and it is thus, like amylose, a true maltosan, but distinguished from amylose by its insolubility in alkali just as amylose is distinguished from dextrin by its insolubility in water Maquenne and Roux[4] also found that the increased activity of malt extract caused by addition of acid also occurs spontaneously on allowing malt extract to stand.

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[1] *Compt. rend.*, 1906, **142**, 95.

[2] *Ibid.*, 1906, **142**, 126.

[3] *Ibid.*, 1906, **142**, 1059.

[4] *Ibid.*, 1906, **142**, 1387.

The properties of amylose and amylopectin appear to account fairly completely for the course of the diastatic hydrolysis of starch. This hydrolysis comprises two reactions of which one, accounting for the saccharification of 80–85 per cent of the starch, is complete in a few hours and represents the conversion of amylose into maltose whilst the other requires several days, progressing at a rate resembling that of the auto-excitation of the malt extract and being perhaps occasioned by this auto-excitation, and represents the conversion of amylopectin into maltose. In the initial stage of diastatic hydrolysis the amylopectin is liquefied and yields the dextrin which remains after saccharification under ordinary conditions. There is an obvious and striking analogy between Maquenne and Roux's scheme of the diastatic degradation of starch, and that put forward by H. T. Brown and his co-workers, but whereas Brown regarded starch as a chemical individual made up of the residues of 80 maltan groups, $C_{12}H_{20}O_{10}$, and 40 dextran groups, $C_6H_{10}O_5$, linked together by oxygen atoms (see p. 20), Maquenne and Roux looked upon starch as consisting of two different substances, of which amylose corresponds to the maltan groups and amylopectin to the dextran groups of Brown.

L. Gatin-Gruzewska[1] showed that the amylopectin constituent of starch forms the envelope of the starch granule and described methods for separating it from amylose and came to the conclusion that it forms 40–45 per cent. of (potato) starch. It was observed by Maquenne[2] that amylopectin, like amylose, cannot be regarded as homogeneous and that there seems to be no sharp distinction between the least soluble amyloses and the least resistant amylopectins; hence starch should contain substances possessing the character, in some degree, both of amylose and of amylopectin. The question of the proportion of these constituents was further investigated by C. Tanret[3] who examined a considerable number of starches and found both constituents in all; the proportion of amylopectin, however, appears to be considerably

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[1] *Compt. rend.*, 1908, **146**, 540.

[2] *Ibid.*, 1908, **146**, 542.

[3] *Ibid.*, 1914, **158**, 1353; **159**, 530.

higher than that found by Gatin-Gruzewska, ranging, according to Tanret from 67 per cent. in chestnut starch to 79·5 per cent. in banana starch. Tanret found that the amylopectin of potato starch dissolves fairly readily in boiling water and that the amyloses of the various starches are not equally soluble.

M. Samec and F. von Hoefft[1] put forward the view that the characteristic properties of starch (e.g. gelatinisation) are due to the presence of an amylophosphoric acid or analogous complex compound of the type $(C_6H_{10}O_5)n$ $(PO_4)yKx$ where K represents a cation, this compound corresponding to the amylopectin of Maquenne and Roux. Thus the amylopectin and amylose fractions of starch were found to contain 0·185 per cent. and 0·007 per cent. of phosphoric anhydride respectively, results which constitute strong evidence that the amylopectin fraction of starch contains the phosphoric acid; the proportions of amylose and amylopectin in starch were found to be 17 and 83 per cent. respectively, the latter figure being higher than any of those found by Tanret in various starches. Samec and H. Haerdtl[2] found that all varieties of starch can be separated by electro-dialysis into an amylopectin fraction which is highly viscous and electro-conducting and an amylose fraction which is non-viscous and non-conducting. If amylopectin is heated with water under pressure, the phosphoric acid is split off, and the carbohydrate thus obtained dissolves in water to a non-viscid solution; this de-phosphorised amylopectin was assigned by Samec[3] to the group of erythroamyloses, and Samec and A. Meyer[4] found that by esterification with phosphoric acid it could be converted back into a product quite similar to amylopectin; amylose also, on conversion into a phosphoric ester, yields a substance of a gelatinous nature. According to Samec, M. Minaeff and N. Ronzin[5] amylopectins of different origins exhibit differences in respect of the appearance and viscosity of their aqueous solutions, conductivity, phosphorus-content, etc.

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[1] *Koll. Chem. Beihefte*, 1912, **4**, 132; 1913, **5**, 141; 1914, **6**, 23, 291.

[2] *Ibid.*, 1920, **12**, 281.

[3] *Ibid.*, 1919, **10**, 304.

[4] *Ibid.*, 1922, **16**, 89.

[5] *Ibid.*, 1924, **19**, 203.

S. B. Schryver and E M. Thomas[1] found that certain starches contain a hemicellulose in proportions ranging from 0 in potato starch to nearly 4 per cent. in sago starch, and according to A. R. Ling and D. R. Nanji[2] who confirmed this observation the ratio of amylose to amylopectin in starches is constant and equal to 2:1 although the absolute percentages of these two constituents may vary according to the proportion of hemicellulose in the starch.

According to T. C. Taylor and H. A. Iddles[3] starch can be separated into its two components amylose and amylopectin (which they designate $\beta$-amylose and $\alpha$-amylose respectively) by disintegration with ammonium thiocyanate solution, and subjection of the product to ultrafiltration or electrodialysis. These workers thus find that maize and rice starches contain 81–88 per cent. of amylose and 12–19 per cent. of amylopectin whilst potato starch contains 97–98 per cent. of amylose and 1·8–2·9 per cent. of amylopectin.

Taylor and L. Lehrmann[4] found that maize starch and other starches (see p. 203) contain small proportions of fatty acids which cannot be removed by solvents and which they consider are combined with the amylopectin constituent of starch.

It will be noticed that very widely discrepant values have been obtained by different workers for the proportions of amylose and amylopectin in starch, the assigned figures ranging from 81–98 per cent. of amylose and 2–19 per cent. of amylopectin (Taylor and Iddles) to 17 per cent. of amylose and 83 per cent. of amylopectin (Samec and von Hoefft); these discordant results are probably due either to defective methods of separation of amylose and amylopectin or to imperfect definition of the two substances.

Of the various compounds formed in the hydrolysis of starch either by acids or by diastase only two—maltose and dextrose—are obtainable in crystalline form; the amorphous gummy nature of the other products has rendered their separation and purification difficult and, in some cases, impossible, and has been responsible in a great degree for the divergent views

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[1] *Biochem. J.*, 1923, **17**, 497.

[2] *Chem. Soc. Trans.*, 1923, **123**, 2666.

[3] *J. Ind. Eng. Chem.*, 1926, **18**, 713.

[4] *J. Amer. Chem. Soc.*, 1926, **48**, 1739.

that have been advanced concerning the constitution of starch and the mechanism of starch hydrolysis. Hence, a discovery, made by F. Schardinger, that starch may be made to yield a number of crystalline compounds by a process of bacterial decomposition has proved of the utmost value for the elucidation of the constitution of starch. Schardinger[1] found that if a mixture of starch paste and mineral nutrient salts is seeded with a culture of *B. macerans* and kept at 45° C., for three or four days, two non-reducing and non-fermentable crystalline dextrins are formed which he named $\alpha$-dextrin and $\beta$-dextrin; both are soluble in water and can be precipitated from aqueous solution by alcohol, ether, chloroform or iodine solution. The two compounds show a striking difference in respect of the addition compounds which they form with iodine; that formed by $\alpha$-dextrin, when seen in a thin layer, is blue in a moist state and greyish-green when dry whereas the iodine compound of $\beta$-dextrin has a brownish colour both when moist and after drying. Schardinger also obtained a third crystalline dextrin by the action of *B. macerans* on starch; it is formed in much smaller quantity than the other two.

These three dextrins were subjected to a thorough investigation by H. Pringsheim and A. Langhans and F. Eissler.[2] It was found that each of the three dextrins has the empirical formula, $C_6H_{10}O_5$, and that they form definite acetyl derivatives which on hydrolysis yield crystalline dextrins isomeric with the dextrins from which they are derived. Thus, Schardinger's $\alpha$-dextrin has the formula $(C_6H_{10}O_5)_4$, and on acetylation and subsequent hydrolysis it yields a dextrin of the composition $(C_6H_{10}O_5)_2$. Schardinger's $\beta$-dextrin has the composition $(C_6H_{10}O_5)_6$, and on acetylation and hydrolysis it yields a dextrin of the composition $(C_6H_{10}O_5)_3$. Schardinger's third dextrin has the composition $(C_6H_{10}O_5)_6$ and is thus structurally isomeric with his $\beta$-dextrin. Pringsheim and Langhans proposed that these dextrins should be called amyloses generically with the specific names, di-, tri-, tetra- and hexa-amylose; they can be separated into two groups or series

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[1] *Zentr. Bakt. u. Parasitenk.*, 1908, II, **22**, 98; 1911, II, **29**, 188.

[2] *Ber.*, 1912, **45**, 2533; 1913, **46**, 2959.

depending on their behaviour towards iodine, those belonging to one series—the α-series—giving iodine addition products in the form of metallic green needles, and those belonging to the other—the β-series—giving brownish-red iodine compounds crystallising in prisms.

**α-series.**

| | |
|---|---|
| Hexa-amylose (Schardinger's third dextrin) | $\{(C_6H_{10}O_5)_2\}_3$ |
| Tetra-amylose (Schardinger's α-dextrin) | $\{(C_6H_{10}O_5)_2\}_2$ |
| Di-amylose | $(C_6H_{10}O_5)_2$ |

**β-series.**

| | |
|---|---|
| Hexa-amylose (Schardinger's β-dextrin) | $\{(C_6H_{10}O_5)_3\}_2$ |
| Tri-amylose | $(C_6H_{10}O_5)_3$ |

The views, expressed in the above formulae, that α-hexa-amylose is a trimeric di-amylose, and β-hexa-amylose a dimeric tri-amylose, were subsequently confirmed by Pringsheim and K. Goldstein[1] from the cryoscopic behaviour of the methyl derivatives of these compounds. Pringsheim and W. Persch[2] found that tetra-amylose and di-amylose can each be methylated to the extent of two methyl groups per glucose residue, the former yielding octamethyl-tetra-amylose and the latter tetramethyl-diamylose.

A striking correspondence between the properties of the amylose of Maquenne and Roux and the α-poly-amyloses of Pringsheim and also between the amylopectin of Maquenne and Roux and the β-poly-amyloses of Pringsheim was pointed out by Pringsheim and Goldstein[3]; this correspondence is confirmed and emphasised by the observation that in the fermentation of amylose and of amylopectin by *B. macerans*, a larger yield of α-poly-amyloses is obtained from the former and of β-poly-amyloses from the latter. It would appear therefore, that Maquenne and Roux's amylose (the interior portion of the starch granule) is built up from a disaccharide unit (di-amylose of the α-series) and that their amylopectin (the envelope of the starch granule) is built up from a trisaccharide unit (tri-amylose of the β-series). This conception of the constitution of starch is in accord with an observation of Pringsheim and Eissler[4] that the acetylation of soluble

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[1] *Ber.*, 1923, **56**, 1520.

[2] *Ibid.*, 1921, **54**, 3162; 1922, **55**, 1425.

[3] *Ibid.*, 1922, **55**, 1446.

[4] *Ibid.*, 1913, **46**, 2959.

starch results in the formation of a trisaccharide group, and with the observation of A. Pictet and R. Jahn[1] who found that on heating potato starch in glycerol at 200–210° C. until it no longer gives a colour with iodine, a trihexosan, isomeric with Pringsheim's tri-amylose, is formed; that no disaccharide or dihexosan was isolated from the reaction products in these cases, is easily explicable if amylose, from which, according to the above conception, these compounds should be derived, is present in starch in much smaller proportion than amylopectin. Further strong support for the view that a disaccharide unit is the basis of Maquenne's amylose and a trisaccharide unit the basis of amylopectin is afforded by the work of Pringsheim and K. Wolfsohn[2] who found that by acetylating amylose and amylopectin the acetates of a disaccharide and a trisaccharide are respectively obtained, and that on heating in glycerol, amylose yields a dihexosan $(C_6H_{10}O_5)_2$ and amylopectin yields Pictet and Jahn's trihexosan $(C_6H_{10}O_5)_3$.

Neither of these hexosans nor any of Pringsheim's polyamyloses possesses reducing power, but Pringsheim and J. Leibowitz[3] found that on treating the polyamyloses with cold, concentrated hydrochloric acid a reducing disaccharide $C_{12}H_{22}O_{11}$ to which they gave the name of amylobiose, is formed; the same sugar is obtained by the action of cold, concentrated hydrochloric acid on amylose or on dihexosan, and another reducing sugar, amylotriose $C_{18}H_{32}O_{16}$, is formed in the same way from amylopectin or from trihexosan.[4] Each of the four sugars, amylobiose, amylotriose, dihexosan and trihexosan, can be quantitatively hydrolysed to maltose by diastase, the relation of each of these compounds to the parent substance, starch, being thus confirmed. Of particular interest is an observation made by Pringsheim and Leibowitz that amylobiose is only hydrolysed by malt diastase and not by pancreatic or saliva diastase, whilst on the other hand dihexosan is quantitatively converted into maltose by pancreatic diastase. These results corroborate the opinion of

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[1] *Helv. Chim. Acta.*, 1922, **5**, 640.

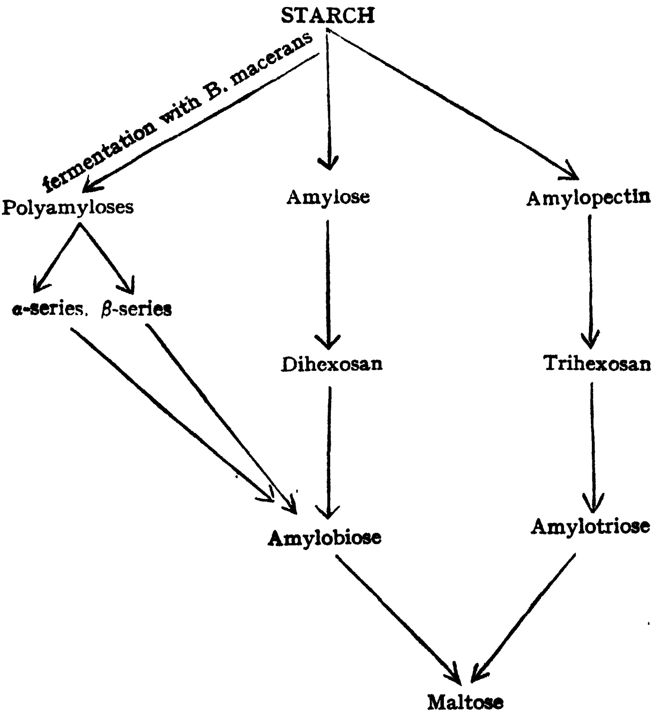
[2] *Ber.*, 1924, **57**, 887.

[3] *Ibid.*, 1924, **57**, 884.

[4] *Ibid.*, 1924, **57**, 1581.

R. Kuhn[1] (see also p. 63) that diastases are divisible into an α- and a β- group, pancreatic diastase belonging to the former and malt diastase to the latter.

The relations between starch, amylose and amylopectin and the derivatives investigated by Pringsheim and his collaborators are shown in the following scheme:—



The properties of amylobiose, amylotriose and the corresponding hexosans appear to correspond with the following structural formulae[2]:—

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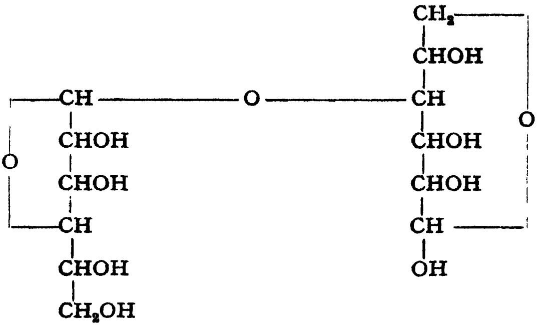
[1] *Annalen.*, 1925, **443**, 1.

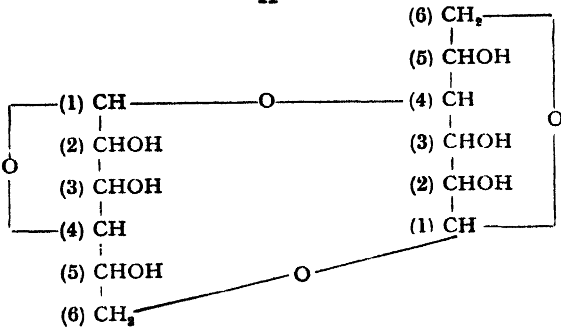
[2] *Pringsheim, Ber.*, 1924, **57**, 1581.

I



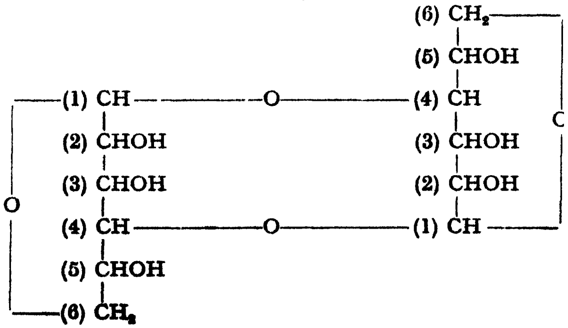
Amylobiose or (1:4) glucosido—4—(1·6) glucose.

II



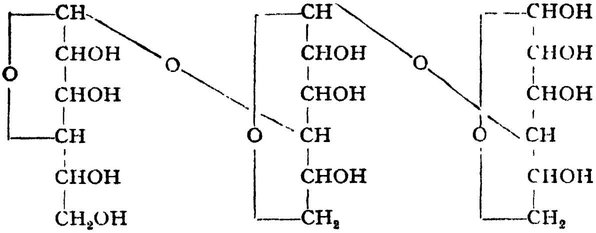
Dihexosan or 6 (1·4) glucosido—4—(1·6) glucoside.

or IIa



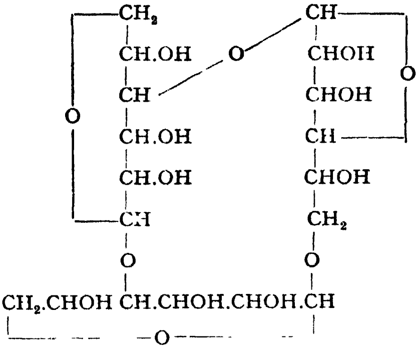
Dihexosan or 4 (1·6) glucoside—4 (1·6) glucoside.

III



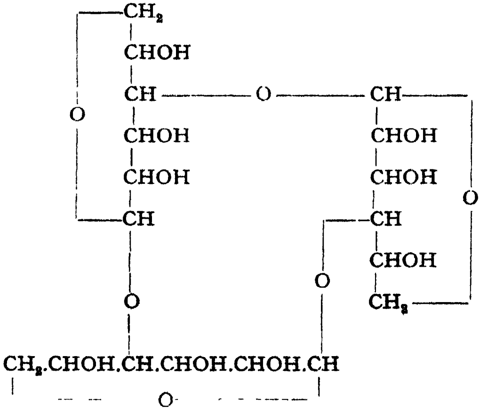
Amylotriose or (1·4) glucosido—4—(1·6) glucosido—4—(1·6) glucose.

IV



Trihexosan or 4(1·6) glucosido—4(1·6) glucosido—6(1·4) glucoside.

or IVa



**Trihexosan or 4 (1·6) glucosido—4 (1·6) glucosido—4 (1·6) glucoside.**

R. Kuhn and W. Ziese[1] have prepared monomethyl trihexosan from Pictet and Jahn's trihexosan and find that it yields 6-methylglucose on hydrolysis whence they conclude that neither of the formulae suggested for trihexosan by Pringsheim can be correct since according to either of these formulae the 6-carbon atom position in the glucose residues is not available for methylation.

The behaviour of starch and of some of its derivatives towards acetyl bromide at the ordinary temperature throws further light on the constitution of starch according to P. Karrer and C. Nägeli.[2] These workers found that Pringsheim's α-tetra-amylose and α-di-amylose and starch itself each yields acetobromomaltose under these conditions. They concluded that α-di-amylose is a maltose anhydride and that, since acetyl bromide does not decompose polysaccharide sugars, *e.g.* sucrose and maltose—at the ordinary temperature, starch does not contain more than two glucose residues joined together by glucoside linkages. Again, since no sugar of greater complexity than maltose is formed in the hydrolysis of starch either by acids or by diastase, and since the α-polyamyloses of Pringsheim are polymers of di-amylose or maltose anhydride (the β-polyamyloses being regarded as secondarily derived from the α-polyamyloses), Karrer and Nägeli further concluded that starch is polymeric maltose anhydride, and that soluble starch and starch dextrins are polymers of maltose anhydride of lower degrees of polymerisation than starch itself. Karrer, Nägeli, O. Hurwitz and A. Walti[3] determined the heats of combustion of maltose, polyamyloses, starch and laevoglucosan and from the results obtained concluded that starch cannot be a higher polymeric form of the α-amyloses than α-octa-amylose and that it is a member of a series of polymers of maltose anhydride or di-amylose isomeric with the α-amyloses. Karrer also found[4] that on dissolving the polyamyloses in dilute sodium hydroxide solution and

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[1] *Ber.*, 1926, **59**, 2314.

[2] *Helv. Chim. Acta.*, 1921, **4**, 169, 185, 263.

[3] *Ibid.*, 1921, **4**, 678.

[4] *Ibid.*, 1921, **4**, 811.

adding alcohol to the solution the following compounds are thrown down:—

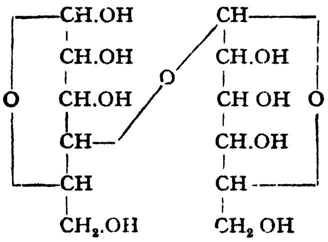
| | |
|---|---|
| Di-amylose-sodium hydroxide | $C_{12}H_{20}O_{10}.NaOH$ |
| α-Tetra-amylose-sodium hydroxide | $(C_{12}H_{20}O_{10}.NaOH)_2$ |
| β-Hexa-amylose-sodium hydroxide | $(C_{12}H_{20}O_{10}.NaOH)_3$ |
| α-Octa-amylose-sodium hydroxide | $(C_{12}H_{20}O_{10}\ NaOH)_4$ |

Soluble starch was found to give a compound of the same percentage composition as those mentioned above.

Karrer regards these results as further evidence for his view that maltose anhydride is the fundamental unit of starch and that the latter is to be regarded as a polymeric form of maltose anhydride.

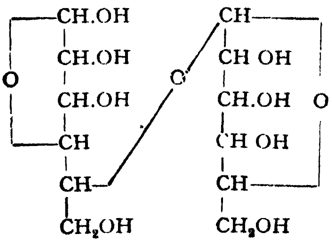
The work of Karrer and his colleagues emphasises the importance of a knowledge of the constitution of maltose as an aid in the elucidation of the nature of starch. This problem has recently been settled by C. J. A. Cooper, W. N. Haworth and S. Peat[1] who have found that heptamethyl methylmaltoside, on hydrolysis yields 2-3-6-trimethylglucose and 2-3-4-6-tetramethylglucose. It follows from these results that maltose must have one of the two alternative formulae:—

I



or

II



Haworth and Peat[2] have brought forward experimental evidence that of these alternatives formula I is probably the correct one, and if, as Karrer and Nägeli contend, Pringsheim's di-amylose is a maltose anhydride, the problem of the constitution of the former, and therewith of starch, resolves itself into a question of the position of the oxygen bridge which is formed in the removal of the elements of water from the maltose molecule.

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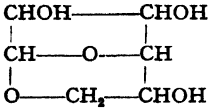
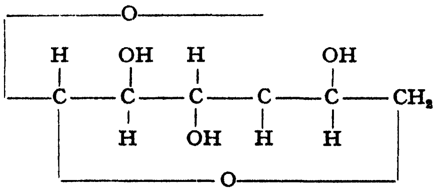
[1] *Chem. Soc. Trans.*, 1926, **129**, 876.

[2] *Ibid.*, 1926, **129**, 3094.

An entirely novel method of attacking the problem of the constitution of starch is that devised by A. Pictet and J. Sarasin[1] who found that if starch or cellulose or dextrin is heated under reduced pressure (12–15 mm.) a large yield (45 per cent.) of laevoglucosan, $C_6H_{10}O_5$, is obtained. Ordinary glucose (*i.e.* α-glucose) when treated in the same way does not yield more than a trace of laevoglucosan, but it was shown by Karrer[2] that β-glucose gives almost as much laevoglucosan as starch; this fact and the observations of Pictet and M Cramer[3] that on treatment with acetyl chloride laevoglucosan forms acetochloroglucose-β show that laevoglucosan is an internal anhydride of β-glucose. The further observation of Pictet and Cramer that on oxidation with potassium permanganate, laevoglucosan gives a diketo-alcohol with the ketonic groups probably adjacent indicates that it has the formula



or arranged spacially thus:



to conform with its derivation from β-glucose. Laevoglucosan is remarkable for the readiness with which it undergoes polymerisation. Pictet[4] found that if laevoglucosan is heated at 180° C. for a few minutes in presence of platinum black, it is converted into tetra-laevoglucosan $(C_6H_{10}O_5)_4$, a white amorphous powder which yields glucose when heated with dilute sulphuric acid; this polymerisation can be effected even more readily if zinc chloride is used instead of platinum black.[5]

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[1] *Helv. Chim. Acta.*, 1918, **1**, 87.

[2] *Ibid.*, 1920, **3**, 258.

[3] *Ibid.*, 1920, **3**, 640.

[4] *Ibid.*, 1918, **1**, 226.

[5] *Ibid.*, 1921, **4**, 788.

Again, Pictet and J. H. Ross[1] found that when laevoglucosan is heated under reduced pressure (15 mm.) it forms di-laevoglucosan $(C_6H_{10}O_5)_2$; when it is heated with a small quantity of zinc chloride and an excess of benzene in a sealed tube (a pressure of 4·6 atmospheres) it forms hexa-laevoglucosan $(C_6H_{10}O_5)_6$, and when it is heated with zinc chloride and excess of ether (13·3 atmospheres), it forms octa-laevoglucosan $(C_6H_{10}O_5)_8$. Thus, these poly-laevoglucosans form a series quite comparable and analogous to that of the poly-amyloses studied by Schardinger, Pringsheim and Karrer. As the degree of polymerisation increases, the polymers approximate more and more in properties to dextrins. More recently, J. C. Irvine and J. W. H. Oldham[2] have obtained tri-, tetra-, and hepta-glucosans by heating laevoglucosan at 250° C. in presence of zinc dust; the tetra- compound, however, is different from that described by Pictet. A. Georg and A. Pictet[3] have found that the di-laevoglucosan formed on heating laevoglucosan under reduced pressure, is an anhydride of isomaltose since on hydrolysis it is converted into isomaltose identical with the compound obtained by E. Fischer by the action of cold concentrated hydrochloric acid on glucose (see p. 20).

Pictet and his co-workers have discovered and investigated yet another polymeric series from starch, *viz.* the hexosans. In addition to dihexosan derived from amylose and trihexosan derived from amylopectin (see p. 31), a hexahexosan $(C_6H_{10}O_5)_6$, is formed as one of the products of heating starch in glycerol at 200°C.[4] This compound is depolymerised on heating with acetic anhydride and sodium acetate, giving the mono-acetate of the trihexosan described by Pictet and Jahn (see p. 31). The trihexosan is hydrolysed by emulsin to glucose and dihexosan[5] from which it may be inferred that trihexosan is a $\beta$-glucosyl dihexosan and that there exists in starch (or rather

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[1] *Helv. Chim. Acta.*, 1922, **5**, 876.

[2] *Chem. Soc. Trans.*, 1925, **127**, 2903.

[3] *Helv. Chim. Acta.*, 1926, **9**, 612.

[4] A. Pictet and P. Stricker, *Helv. Chim. Acta.*, **1924**, **7**, **932**.

[5] A. Pictet and R. Salzmann, *Helv. Chim. Acta.*, **1924**, **7**, **934**; **P. Castan and** A. Pictet, *Helv. Chim. Acta.*, 1925, **8**, 946.

in amylopectin from which trihexosan is derived) a glucosyl radicle united to the rest of the molecule by a β-linkage; no doubt the presence of this group is responsible for the formation of laevoglucosan when starch is distilled *in vacuo*, and for the formation of isomaltose which has been frequently observed in the hydrolysis of starch by ferments. In the course of the action of emulsin on trihexosan, a tetra-hexosan is also formed (evidently by polymerisation of the dihexosan formed in the first instance).[1] Dihexosan yields β-octacetyl maltose on acetylation and is, therefore, like diamylose, one of the several theoretically possible maltose anhydrides.

The four polymeric hexosans, *viz.* di-, tri-, tetra-, and hexahexosan, may be regarded as successive products of condensation of a single hypothetical monohexosan, $C_6H_{10}O_5$, These compounds have the following constants.[2]

TABLE II.

| | Specific Rotation $[\alpha]_D$ | Molecular Weight M | Molecular Rotatory Power $\frac{[\alpha]_D M}{100}$ |
|---|---|---|---|
| Dihexosan $(C_6H_{10}O_5)_2$ | + 132·2° | 324 | 432° |
| Trihexosan $(C_6H_{10}O_5)_3$ | + 154·3° | 486 | 749° |
| Tetrahexosan $(C_6H_{10}O_5)_4$ | + 162·6° | 648 | 1067° |
| Hexahexosan $(C_6H_{10}O_5)_6$ | + 173·2° | 972 | 1703° |

In this series the addition of each glucose group increases the molecular rotatory power by the same amount and if, as Pictet considers very probable,[3] soluble starch is a higher member of the same series, the number of glucose groups in its molecule should be determinable from its molecular rotatory power. The specific rotatory power of soluble starch, however, has not been determined accurately, the values assigned by different chemists ranging from $[\alpha]_D = 186°$ to 202°. It may be concluded therefore, that the soluble starch preparations obtained by various methods (see pp. 54–56) have been mixtures, in different proportions, of products of the more or less complete disaggregation of starch. A large proportion of the values assigned as the specific rotatory

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[1] A. Pictet and R. Salzmann, *Helv. Chim. Acta.*, 1925, **8**, 948.

[2] A. Pictet, *Helv. Chim. Acta.*, 1926, **9**, 33.

[3] *Loc. cit.*

power, however, approximate to 189°, and assuming this to be the specific rotatory power of a definite compound, extrapolation from the molecular rotatory powers given in the above table indicates that this definite compound should have the formula $(C_6H_{10}O_5)_{18}$ and $[\alpha]_D = 192°$, a figure which agrees sufficiently well with the experimental approximation to render probable the conclusion that in the mixture of products of disaggregation of starch known as soluble starch there is one compound of formula $(C_6H_{10}O_5)_{18}$ and specific rotatory power about 189.

Quite recently A. R. Ling and D. R. Nanji[1] have attacked the problem of the constitution of starch by enzymic hydrolysis both of starch itself and of its constituents under various conditions. Thus they found that the amylose of Maquenne and Roux, on treatment with barley or malt diastase is rapidly and completely converted into maltose, and they regard amylose as having $\alpha$-hexa-amylose as basal unit. Maquenne and Roux's amylopectin, on the other hand, when treated with barley diastase, is de-phosphated and converted into $\alpha\beta$-hexa-amylose, and the latter is regarded by Ling and Nanji as the basal unit of amylopectin. $\alpha\ \beta$-Hexa-amylose, on hydrolysis with malt diastase, was found by Ling and Nanji to yield products the nature of which depends on the conditions under which hydrolysis is effected. Thus, if malt diastase is allowed to act on $\alpha\beta$-hexa-amylose at 70° C. malto-dextrin-$\alpha$ (previously isolated by Ling and Baker, see p. 22) and $\beta$-glucosidomaltose are successively formed and the latter yields a mixture of maltose, glucose and isomaltose. If malt diastase is allowed to act on $\alpha\ \beta$-hexa-amylose at 55° C. maltose and isomaltose are obtained as final products, but the proportions of these two sugars and the nature of the intermediate products depend on the presence or absence of maltose initially; thus, if maltose is added at the beginning of the reaction, the stable dextrin of Brown and Morris (see p. 19), which appears to be a mixture of Ling and Baker's malto-dextrin-$\beta$ (see p. 22) and a closed chain substance, is formed intermediately, whilst the ratio of the final products, maltose

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[1] *Chem. Soc. Trans.*, 1923, **123**, 2666; 1925, **127**, 629, 636.

and isomaltose, depends on various factors but does not exceed 2:1; if no maltose is added initially, maltodextrin-$\beta$ is formed intermediately, whilst the ratio of maltose and isomaltose is 1 : 2.

The problem of the nature of starch has also been investigated by J. C. Irvine and J. Macdonald[1] who have successfully applied the method of exhaustive methylation that has proved so valuable in elucidating the constitution of the sugars. This method consists essentially in methylating starch, and decomposing the methylated product into the corresponding methyl glucose or methyl glucoses; the position of the methoxyl groups in the glucose molecule should correspond to the position of the free hydroxyl groups in the starch molecule. Irvine and Macdonald found that starch can be methylated in three stages which are so definite that it is justifiable to conclude that each stage corresponds to a distinct compound. In the first stage, effected with methyl iodide and silver oxide, a product containing 32 per cent. of methoxyl, corresponding to a dimethyl starch is obtained; this product yields a dimethyl glucose on hydrolysis. In the second stage, effected by four successive treatments of starch with methyl sulphate and alkali hydroxide a product containing 37 per cent. of methoxyl is obtained; this proportion of methoxyl corresponds with the assumption that of three hexose residues in starch one has combined with three methyl groups and the other two have each combined with two methyl groups. That such is the case is borne out by the observation that the product yields 2-3-6-trimethylglucose (1 mol.) and a dimethylglucose (2 mols.) on hydrolysis. In the third stage of methylation, which is only attained after many repetitions of the methylating process, a product is obtained containing 43·7 per cent. of methoxyl and corresponding closely with the composition of a trimethyl starch. This substance on hydrolysis yields 2-3-6-trimethylglucose as sole product. The yield of 2-3-6-trimethyl glucose corresponds to about 60 or 70 per cent. of the starch and it may therefore be concluded that starch is largely, if not entirely built up of glucose residues in which

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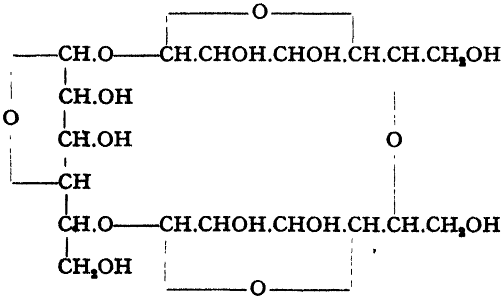
[1] *J. Soc. Chem. Ind.*, 1922, **41**, 363R; *Chem. Soc. Trans.*, 1923, **123**, 898; 1926, **129**, 1502.

the hydroxyl groups joined to carbon atoms, 2, 3 and 6 remain free in the starch molecule.[1]

It has also been shown by Irvine, Pringsheim and Macdonald[2] that β-hexa-amylose, on exhaustive methylation, yields β-hexa-trimethyl-amylose $\{C_6H_7O_5(CH_3)_3\}_6$, and that on hydrolysis the latter yields the same sugar, *viz.*, 2-3-6-trimethylglucose, as is obtained from fully methylated starch. Again the trihexosan obtained by the depolymerisation of starch,[3] on methylation and hydrolysis also yields 2-3-6-trimethylglucose and, as observed by Cooper, Haworth and Peat (see p. 36) heptamethylmaltose yields the same sugar and 2-3-4-6-tetramethyl glucose on hydrolysis. These results of course, confirm the view that the hydroxyl groups attached to carbon atoms 2, 3 and 6 of the glucose residues in the starch molecule are free.

Irvine and Macdonald point out that the formation of a definite compound containing 37 per cent. of methoxyl in the course of the methylation of starch throws light on the constitution of the latter. This methylated starch on hydrolysis yields exactly one molecule of 2-3-6-trimethylglucose and two molecules of dimethylglucose, and therefore it follows that the molecular unit of starch must contain either 9 or a multiple of 9 hydroxyl groups and the simplest possible unit must be a trihexosan to which the formula:—



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[1] It is noteworthy that 2-3-6-trimethylglucose was isolated by Denham and Woodhouse from the products of hydrolysis of methylated cellulose (see *Chem. Soc. Trans.*, 1914, **105**, 2357). This indicates the very close chemical relationship between cellulose and starch.

[2] *Chem. Soc. Trans.*, 1924, **125**, 942.

[3] Pictet and Jahn, *Helv. Chim. Acta.*, 1922, **5**, 640, see p. 31.

may be ascribed. In view of the existence of poly-amyloses containing an even number of $C_6$-chains, however, it is probable that the basal unit of unpolymerised starch has twice this magnitude, i.e. that it consists of a ring structure of six glucose residues, *i.e.* a hexa-hexosan.

It is evident, from the preceding necessarily rather involved account of research on the constitution or composition of starch, that there has been and still exists a wide diversity of opinion as to the nature of this substance, even its claim to be regarded as a single chemical compound being still in dispute. The view of H. T. Brown and his co-workers that starch is a chemical individual of the formula 100 $C_{12}H_{20}O_{10}$, made up of 80 maltan groups, $C_{12}H_{20}O_{10}$, and 40 dextran groups, $C_6H_{10}O_5$, linked in ring formation by oxygen atoms, conflicts with the view of Maquenne and Roux that starch consists of two different substances of which one, amylose, constitutes the internal portion of the starch granule whilst the other, amylopectin, forms the external layer. There is a certain resemblance or analogy between these two views if the amylose is regarded as corresponding to the maltan groups and the amylopectin to the dextran groups of Brown, but a quantitative correspondence would require that the amylose and amylopectin should be present in starch in the proportion of 4 to 1. The values assigned by different workers to the proportion of amylose to amylopectin in starch are so widely divergent, however (see p. 28), that it seems impossible in the present state of our knowledge to form even an approximate estimate. Maquenne and Roux's theory of the dual nature of starch is supported by the experimental evidence of Samec and others according to which amylopectin owes its characteristic properties to the presence of a phosphoric acid complex; the amount of phosphoric acid in amylopectin is very small, however (see p. 27), and if it forms an integral part of the amylopectin molecule the magnitude of the latter must be at least about 70,000. The amylose-amylopectin theory of the composition of starch finds further support from the work of Schardinger and of Pringsheim and others on the crystalline $\alpha$- and $\beta$-amyloses, and if, as is claimed, Maquenne's amylose is built of α-diamylose units and amylopectin is built of β-triamylose units, the intricate problem of the nature of starch is not far from being solved.

The observation, on the other hand, that the sugars, amylobiose and dihexosan, which are derived from amylose, and the sugars amylotriose and trihexosan which are derived from amylopectin, can all be quantitatively hydrolysed to maltose by diastase, is strong evidence of the persistence and stability of the maltose complex in the degradation products of starch. The formation of maltose in these cases accords rather strikingly with the results obtained by Karrer and others according to whom starch is polymeric maltose anhydride, soluble starch and starch dextrins being lower polymers of the same substance. Karrer's view that maltose anhydride is the unit from which starch is built seems quite consistent with the observation of Pictet and his colleagues that starch yields a large proportion of laevoglucosan when heated under reduced pressure. If, as is probable, maltose is a sugar of the β-glucose type, maltose also should yield laevoglucosan when heated under suitable conditions. Further, the work of Pictet and his colleagues on the series of polymeric hexosans obtained by heating starch in glycerol would appear to indicate that dihexosan which is a maltose anhydride, is the maltose anhydride from which, according to Karrer, the starch molecule is built up. Both Karrer and Pictet appear to regard starch as a single chemical compound but the view that it consists of the two substances, amylose and amylopectin is supported by Ling and Nanji who regard the former as built up from α-hexa-amylose and the latter from α-β-hexa-amylose.

The work of Irvine and Macdonald on the methyl derivatives of starch and their products of hydrolysis appears to settle the constitution of the glucose residue or hexosan which forms the fundamental unit of starch but does not settle the question of the single or dual nature of starch since the methylated products obtained by them only account for about 60 or 70 per cent. of the starch. The conclusion of Irvine and Macdonald that the basal unit of starch is a hexa-hexosan accords with the view of Ling and Nanji mentioned above.

# CHAPTER IV.

# PROPERTIES OF STARCH

PURE starch is a perfectly odourless and tasteless white powder; commercial starches are quite or almost white, though wheat starches sometimes exhibit a faint greyish, and potato starches a faint yellowish tinge. Starch is stable in the air at ordinary temperatures and when dry may be heated to well over 100° C. without change. At 150–160° C. it turns slightly yellow and becomes soluble in water, being converted into dextrin. On heating with water in a sealed tube at 200° C., starch yields pyrocatechol amongst other products.[1]

The density of starch varies according to the amount of moisture present. According to E. Parow[2] the densities of the more important starches in the dry state are as follows:—Potato starch, 1·648; wheat starch, 1·629; maize starch, 1·623; rice starch, 1·620 at 17·5°/17·5° C.

The refractive indices of different starches show slight differences, ranging for the air-dry starch, according to E. Ott[3] from 1·504 (Fritillaria starch) to 1·529 (tapioca starch).

The rotatory powers of different starches in the gelatinised state appear to differ slightly, ranging from $[\alpha]_D$ 201·5° for maize starch to 204·3° for potato starch; in view of the difficulty of obtaining accurate readings it is unlikely that such small differences have any significance.

Pure starch is quite neutral but commercial starches are generally slightly acid and occasionally slightly alkaline.

Starch is quite insoluble in cold water and in all organic solvents. If, however, it is ground with water, the filtered liquid gives the characteristic blue colour with iodine, but

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[1] F. Hoppe-Seyler, *Ber.*, 1871, **4**, 15.

[2] *Zeitsch. Spiritusind,.* 1907, **30**, 432.

[3] *Oesterr. bot. Zeitsch.*, 1899, **49**, 313.

it is not clear whether this is due to actual solution of the interior part of the broken granules or to slight gelatinisation owing to heat engendered in grinding, or to fine particles of the granules too small to be retained by the filter. According to C. L. Alsberg[1] if natural starch is ground in a pebble mill until most of the granules, though still recognisable under the microscope as starch, are injured, the starch becomes incapable of gelatinisation at ordinary concentrations. A large proportion of the substance of the starch granules becomes colloidally soluble in cold water. Such ground starch yields clear solutions with cold water which give the iodine reaction, do not reduce Fehling's solution and dialyse through thin collodion membranes. In view of the probability that the starch granule consists of a more or less soluble interior portion —amylose—contained in an insoluble envelope—amylopectin —(see p. 26) it may be that the cold aqueous solution obtained from ground starch is a solution of amylose.

Dried starch is very hygroscopic and air-dried starch contains a considerable amount of water, varying with different starches; thus, wheat and maize starches contain about 13 per cent. whilst potato starch contains 18–20 per cent. It is very difficult to expel the water entirely and according to Bloch,[2] starch must be heated to 155–160° C. to remove the last traces of water. If dried or partly dried starch is mixed with water a very perceptible rise in temperature occurs. F. Ullik found[3] that on mixing air-dried potato starch with an equal weight of water the temperature rose by 3° C., whilst if the starch had been previously dried at 120° C., a rise of temperature of 13·8° C. was obtained. Starch which has been exposed to an atmosphere saturated with moisture at the ordinary temperature may contain as much as 35–37 per cent. of water.

*Gelatinisation.*—If an aqueous suspension of starch is heated or if starch is mixed with hot water, the granules swell enormously and finally burst, the mixture forming the viscid, cloudy liquid known as starch paste. The temperature at

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[1] *J. Ind. Eng. Chem.*, 1926, **18**, 190.

[2] *Compt. rend.*, 1894, **118**, 146.

[3] *Zeitsch. ges. Brauw.*, 1891, **14**, 565.

which this change occurs is known as the gelatinisation temperature and if, in the course of heating a starch suspension, drops of the liquid are withdrawn at intervals and observed under the microscope with crossed Nicol prisms (see p. 76) it will be found that at, or in the neighbourhood of, the gelatinisation temperature the characteristic interference crosses, due to anisotropy, disappear. The gelatinisation temperature varies with different starches, ranging from about 55 to 85° C., and it has been used as an aid in discriminating between different starches although, as will be seen, it is a criterion of rather doubtful value.

The figures given by various workers for the gelatinisation temperatures of the different starches vary widely owing partly to differences in the methods and rates of heating the starch suspensions and partly to differences in fixing the point at which the interference crosses are considered to disappear some workers taking the temperature as that at which anisotropy disappears from the majority of the granules, whilst others regard it as that at which anisotropy disappears from all the granules. C. K. Francis and O. C. Smith[1] devised an apparatus for carrying out the determination of gelatinisation temperature under uniform conditions and continuous microscopic control. A small quantity of the starch is mixed with excess of water on a "thermoslide" which is heated by a current of hot water of known and increasing temperature, the gelatinisation point being observed under the microscope. A. W. Dox and G. W. Roark[2] adopted the same principle of continuous microscopic observation but used electrical heating instead of a current of hot water. According to their method a small quantity of the starch is placed on a cover glass and moistened with a drop of water, the glass then being placed over the depression in a hanging drop slide. The slide is placed in a "No. 8 electric incubator for the microscope stage" which has previously been brought to a suitable temperature, e.g., 60° C., the slide being kept from contact with the bottom of the chamber by two small rods on which it rests. The microscope is then focussed on the starch and the temperature

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[1] *J. Ind. Eng. Chem.*, 1916, **8**, 509. [2] *J. Amer. Chem. Soc.*, 1917, **39**, 742.

slowly raised until anisotropy has disappeared from all the granules that are large enough to show the characteristic shape and markings. After this test, which serves as a preliminary, the determination is repeated, the initial temperature of the chamber being adjusted to 5° below the gelatinisation point found in the preliminary test, and this temperature then being raised at the rate of 1° per minute. Since the temperature of the chamber varies at different points the correction must be made by determining the melting points of well-known substances under the same conditions. The results obtained by this method show that with any one sample of starch the maximum and minimum values of half a dozen determinations do not differ by more than 0·5° C. This degree of accuracy would suffice in many cases for discriminating between different starches were it not for the fact that starches of the same kind but differing merely in respect of size of granules may show a considerable difference in gelatinisation temperature. Nägeli observed that the larger granules of potato starch begin to gelatinise at 55° C., whereas the smallest granules do not begin to gelatinise until a temperature of 65° C. is attained, and from observations of R. Whymper[1] it would appear that the larger granules of any given starch gelatinise at a lower temperature than the smaller ones. Further, starches from different varieties of the same species of plant may show considerable differences in respect of gelatinisation. Dox and Roark[2] found that the gelatinisation temperatures of thirteen varieties of maize starch ranged from 64·1 to 71·1° C. It is evident that, apart from any other purpose it may serve, a determination of gelatinisation temperature is not of much value for identifying different starches.

The gelatinisation temperature of starch is considerably lowered by alkalis and certain salts. Thus, S. A. Levites[3] found that maize starch, which gelatinises at 66–68° C. in water, gelatinises at 46–48° C. in a 10 per cent. solution of ammonium or potassium thiocyanate or a 20 per cent. solution of sodium

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[1] Seventh Int. Congr. Appl. Chem., London, 1909. VIa, 7.
[2] *J. Amer. Chem. Soc.*, 1917, **39**, 742.
[3] *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 110.

or potassium iodide, and at 52–54° C. in a 20 per cent. solution of sodium or potassium bromide or ammonium nitrate; it gelatinises at the ordinary temperature in a 15–20 per cent. solution of ammonium or potassium thiocyanate or a 40 per cent. solution of sodium or potassium iodide or a 50–60 per cent. solution of sodium or potassium bromide. Di- and trihydric phenols exert a similar influence on gelatinisation.

A. Reychler[1] observed that starch is rapidly gelatinised at the ordinary temperature by sodium or potassium hydroxide solution but not by ammonia; if a 0·75 per cent. solution of potassium hydroxide is used, gelatinisation is slow enough for observation under the microscope. The following substances, at the concentrations stated, have the same influence on the gelatinisation of starch as 0·75 per cent. solution of potassium hydroxide:—Sodium hydroxide, 0·53; potassium iodide, 26–28; ammonium nitrate, 30–35; silver nitrate, 29; potassium thiocyanate, 12–15; and chloral hydrate, 55 per cent.

Gelatinised starch or starch paste is widely used in the textile industry for sizing and stiffening cloth and for these purposes the starch which yields the stiffest, most viscous paste or jelly is the most valuable. H. T. Brown and J. Heron[2] found that the viscosity of a starch paste is much affected by the treatment to which the starch has previously been subjected, being greatly diminished if the starch has been treated with alkali and acid in the process of purification. Again, starch that has been dried slowly at a low temperature gives a more viscous paste than if dried quickly at a higher temperature; thus, Brown and Heron found that potato starch dried first *in vacuo* and then at a temperature not exceeding 30° C., yielded a paste more than three times as viscous as that made from the same kind of starch dried whilst very moist at 50° C. and afterwards at 100° C.

A rough idea of the stiffness or viscosity of the paste from a sample of starch is afforded by the sense of touch, but W. F. A. Ermen[3] found that direct determinations of viscosity

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[1] *Bull. Soc. chim. Belg.*, 1920, **29**, 118.

[2] *Chem. Soc. Trans.*, 1879, **35**, 614.

[3] *J. Soc. Chem. Ind.*, 1907, **26**, 501.

do not give constant results and he proposed to use solutions of starch prepared in the cold with sodium hydroxide, the procedure being as follows:—

230 c.c. of cold water are placed in a wash bottle and the weighed quantity of starch (1–2·5 grms.) washed with this water into a 250 c.c. flask and shaken until an even suspension results; 15 c.c. of 10 per cent. solution of sodium hydroxide are then quickly run in from a burette and the flask filled with cold water to the mark and shaken continuously until the solution begins to thicken. The solution is generally ready for use in a couple of hours, but it is best left until the next morning the viscosity then being determined at some standard temperature in a Redwood viscometer. The method gives concordant results with the same sample of starch whilst different starches and different brands of the same starch are easily distinguished.

An exhaustive study of the viscosity of starch paste and of the conditions affecting it has been made by W. Harrison.[1] In each experiment, 2·5 grms. of dry starch were made up to 250 c.c. with distilled water and boiled under a reflux with a direct flame, or in some cases heated in a boiling water-bath. At certain intervals 25 c.c. of the liquid were withdrawn, transferred to a small flask and rapidly cooled. The viscosity was then determined by noting the time taken by a definite volume of the liquid to flow through a capillary tube compared with the time for the same volume of water all readings being taken at 16° C. The results, and the degrees of concordance obtained are shown in Table III, slightly abridged from the original.

As the table shows, the results obtained with wheat, rice, maize and sago were fairly concordant, and excepting in the case of sago, exhibited a slight increase in viscosity with the duration of heating. Potato starch paste is distinguished by its very high viscosity and it acquires its maximum viscosity in the course of 10–20 minutes heating, a fact of practical importance in connection with the preparation of finishing pastes. The results quoted in the table also indicate, however,

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[1] *J. Soc. Dyers and Col.*, 1911, **27**, 84.

## TABLE III.

VISCOSITY OF STARCH SOLUTIONS (WATER = 1).

| Starch. | Wheat. | | Rice. | | Maize. | | Sago. | | Potato. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature of treatment. | 100° C. | | 100° C. | | 100° C. | | 94°C. | 100°C | 94° C. | | | 100° C. | | | |
| Time of treatment. | | | | | | | | | | | | | | | |
| 5 min. | 1·27 | 1·27 | 2·07 | 2·20 | 2·35 | 2·32 | 3·51 | 3·59 | 30·0 | 30 | 52 | 22·0 | 45 | 59 | 54 |
| 10 ,, | 1·28 | 1·29 | 2·08 | 2·22 | 2·42 | 2·46 | 3·51 | 3·61 | 48·0 | 36 | 71 | 22·5 | 46 | 65 | 60 |
| 15 ,, | 1·28 | 1·29 | 2·11 | 2·26 | 2·51 | 2·52 | 3·51 | 3·51 | 54·5 | 69 | 88 | 23·0 | 46 | 37 | 31 |
| 20 ,, | 1·29 | 1·29 | 2·12 | 2·30 | 2·64 | 2·64 | 3·51 | 3·49 | 60·0 | 98 | 78 | 21·5 | 36 | 44 | 38 |
| 25 ,, | 1·29 | 1·29 | 2·17 | 2·32 | 2·70 | 2·70 | 3·51 | 3·44 | 63·0 | 59 | 63 | 20·0 | 29 | 27 | 21 |
| 35 ,, | 1·30 | — | 2·20 | 2·34 | 2·85 | 2·86 | 3·49 | — | 56·0 | 54 | 48 | 14·5 | 32 | 26 | 22 |
| 45 ,, | 1·30 | — | 2·26 | 2·34 | 2·97 | 3·00 | 3·48 | 3·17 | 49·5 | 50 | 39 | 13·5 | — | — | 14 |
| 60 ,, | — | 1·30 | 2·32 | 2·34 | 3·17 | 3·19 | 3·36 | 3·00 | 28·5 | 38 | — | 12·5 | 24 | 23 | 11 |
| 2 hours | — | 1·29 | — | — | 3·28 | 3·28 | — | 2·54 | — | — | — | — | — | — | — |
| 4 ,, | — | 1·26 | — | — | 3·41 | 3·41 | — | — | — | — | — | — | — | — | 6·7 |
| 6 ,, | — | 1·24 | — | — | 3·50 | 3·53 | — | — | — | — | — | — | — | — | — |
| 8 ,, | — | 1·20 | — | — | — | — | — | — | — | — | — | — | — | — | 2·5 |

that the rate of increase and subsequent decrease of viscosity of a given potato starch paste may be very irregular. Harrison found that the viscosity of a potato starch paste is diminished to a remarkable degree by merely shaking the liquid, owing to disruption of the swollen granules, and he suggested that the peculiarity of potato starch paste in this respect may be due to the comparatively large size of the granules of potato starch. The effect of shaking on the viscosity is so striking that slight variations in the mode of boiling a potato starch paste would easily account for the irregularities shown in the above table, and so far as potato starch is concerned an accurate direct determination of viscosity does not appear to be practicable. The viscosity of a starch paste, however, should be proportional to the swelling of the granules and Harrison has devised a method of determining the degree of swelling from which the viscosity may be calculated by a formula. The method depends on the fact that if starch suspensions are heated to a temperature just above the gelatinisation point and the paste is then cooled, the swollen granules can be separated by centrifuging, and the volume occupied by the granules can be read directly if a graduated tube is used. Harrison found that the volume of the granules is directly proportional to the viscosity no matter what starch is used and that the relation between viscosity and the volume of the swollen granules is expressed by the equation

$$\text{Viscosity} = 1 + \left(4{\cdot}75 \times \frac{\text{Vol. of granules.}}{\text{Total vol. of solution}}\right)$$

The volume occupied by the swollen granules is proportional to the amount of starch used unless the volume approaches 100 per cent. of the total volume. Since the viscosity of a starch paste increases much more rapidly than the proportion of starch (except for low values of the latter), it is probable that the stiffening power of a starch paste is more accurately represented by the volume of the swollen granules than by the viscosity. Since different starches gelatinise at different temperatures and the stiffness of a paste depends on the time during which the starch has been heated, the method cannot be used for the quantitative comparison of stiffening powers of different kinds of starch. For comparing samples of the same kind of starch 1 per cent. suspensions of each are heated simultaneously on the water-bath to a few degrees above the gelatinisation point with careful mixing but not with shaking. The solutions are then cooled, and 15 c.c. transferred to the graduated tube and centrifuged; the volumes of the granules represent the comparative stiffening powers of the starches. If the starch suspensions are heated too long or if they are shaken, the swollen granules may become disintegrated so that the finer particles cannot be separated by centrifuging. In the case of potato starches, owing to the wide range in size of the granules, the comparison must be repeated several times.

F. D. Farrow and G. M. Lones[1] found that the viscosity of potato starch paste at 90° C. increases proportionally with increasing concentration of starch up to about 0·7 per cent. and then increases more rapidly than the concentration. Maize starch pastes show similar behaviour save that the rapid increase in viscosity does not occur until the concentration exceeds 1·5 per cent. O. S. Raske and C. L. Alsberg[2] found that the viscosity of wheat starch paste (measured at 90° C.) varies widely according to the variety of wheat from which the starch has been obtained. Starches from winter wheats yield more viscous pastes than those obtained from spring wheats. Durum and Kansas hard red winter wheats, the starches of which yield pastes of high viscosity, are especially suitable for the manufacture of macaroni, and Raske and Alsberg suggest that the superiority of these wheats in this respect may be due to their starches as well as to their proteins, and that the value of a flour for making macaroni may be ascertained by determining the viscosity of its starch paste.

E. H. Harvey[3] found that cassava starch paste is distinguished by its very high viscosity, but that it rapidly becomes much less viscous on continued heating.

The viscosity of starch paste appears to be greatly affected by the presence of minute quantities of certain salts and the authors have found that with potato starch paste such small

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[1] *J. Text. Inst.*, 1923, **14**, 414.

[2] *Cereal Chem.*, 1924, **1**, 7.

[3] *Amer. J. Pharm.* 1924, **96**, 752.

quantities of salts as are present in most tap waters are sufficient to lower the viscosity very markedly.

*Soluble Starch.*—By appropriate treatment starch is rendered soluble in hot water to a fairly transparent, mobile liquid and of the methods proposed for this purpose, that of C. J. Lintner[1] is the best known and most commonly used. According to this method prime potato starch is mixed with a 7·5 per cent. solution of hydrochloric acid (1 vol. conc. acid to 3 vols. water) so that it is completely immersed, and left for about 7 days at the ordinary temperature or for 3 days at 40° C., by which time the starch has lost its gelatinising power although its microscopic appearance is practically unchanged. It is then washed with water until quite free from acid, treated with one or two drops of dilute ammonia and finally filtered and air-dried at room temperature. The product dissolves to a clear solution in hot water and a 2 per cent. solution will remain clear or only faintly opalescent for some days.

J. S. Ford[2] has observed that potato starch is the most suitable raw material for the preparation of soluble starch by Lintner's method; maize, wheat, rice and barley starches, owing to the smallness of their granules, subside rather slowly from aqueous suspension, and this behaviour prolongs the washing process unduly. Ford recommends that the starch should first be washed with water, then with a 0·5 per cent. solution of soda, and finally with water again before it is subjected to the treatment with acid. Soluble starch intended for the determination of the diastatic power of malt, etc., must of course be neutral. It seems impossible to remove the last trace of acid from starch by repeated washing with distilled water since the starch may still be acid although the wash water therefrom is neutral. If tap water is used for washing after the treatment with acid, the acidity becomes neutralised but there is danger in this case of overshooting the mark and obtaining an alkaline or potentially alkaline product. After using tap water for washing, Ford recommends that the starch should be further washed with distilled water, until a portion dissolved in boiling, neutral water gives

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[1] *J. pr. Chem.*, 1886, **34**, 378.

[2] *J. Soc. Chem. Ind.*, 1904, **23**, 414.

no reaction or, at most, only a faintly acid reaction to rosolic acid. Soluble starch made by the action of hydrochloric acid of sp. gr. 1·037 on starch for 2–3 days at 40° C., may have a copper-reducing power equal to 2–3 per cent. of maltose; if the acid is allowed to act on the starch at the room temperature, products of reducing power as low as 0·2–0·5 per cent. of that of maltose are obtained but they are not so satisfactory for determinations of diastatic power as those of higher reducing power.

J. Wolff and A. Fernbach[1] obtained soluble starch as follows: Starch is treated with hydrochloric acid of 0·1 per cent. concentration at room temperature for 15–30 minutes, washed with distilled water, and dried at about 30° C. The product is then rendered soluble by heating to 46° C. for 8–10 days, or to 100–110° C. for 1½ hours; even if left unheated, it slowly changes to the soluble form. The microscopic appearance of the granules is not altered by the treatment; if the starch is only heated to 46° C. neither reducing sugar nor dextrin is formed and even if it is heated to 100° C. only mere traces of these substances are produced. According to L. Mathieu,[2] soluble starch prepared by Wolff and Fernbach's method gives greater precision as an indicator for titrations with iodine than any other form of soluble starch; the material keeps indefinitely in the dry state and the indicator is prepared from it by boiling 1 grm. with 100 c.c. water and filtering.

A. Reychler[3] has described a method of preparing soluble starch which depends on the use of an oxidising agent. Starch (100 parts) is treated with a 0·75 per cent. solution of potassium dichromate in $N/4$ hydrochloric acid (130–150 parts) for 20 hours. The dichromate is then reduced with sulphurous acid and the starch filtered off, washed and dried at a low temperature. Potassium permanganate may be used instead of dichromate if desired. The product swells but does not dissolve in boiling water; on addition of a trace of alkali or even ammonia or ammonium carbonate, the mucilage is rapidly transformed into a limpid solution which is absolutely

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[1] *Compt. rend.*, 1905, **140**, 1403.

[2] *Ann. Chim. anal.*, 1911, **16**, 51.

[3] *Bull. Soc. chim. Belg.*, 1923, **32**, 221.

free from microscopic particles. The solution has only slight reducing power and has a specific rotation of $[\alpha]_D$ = about 200°.

Other methods of preparing soluble starch have been described by K. Zulkowski,[1] W. Syniewski,[2] Welwart,[3] A. Fernbach[4] and P. Petit.[5]

The specific rotation of soluble starch varies considerably according to the method of preparation, values ranging from $[\alpha]_D + 186$ to $+ 202°$ having been obtained. A. Pictet[6] has observed that most of the values approximate to 189° and he has suggested that in the various mixtures known as soluble starch there is a definite compound $(C_6H_{10}O_5)_{18}$, of approximately this specific rotation.

## HYDROLYSIS OF STARCH.

Starch is hydrolysed on heating with dilute mineral acid or by the action of the enzyme diastase. The products obtained in the two cases are not the same and since the mechanism of the intermediate stages is also probably not similar, the two methods of hydrolysis must be considered separately.

*Acid hydrolysis.*—As long ago as 1812, Kirchoff[7] found that starch, when boiled with dilute sulphuric acid is converted into glucose, an observation which led to the foundation of an important industry (see p. 198). F. Salomon[8] found that complete conversion of starch into glucose may be effected by Sacchse's method according to which 2–2·5 grms. anhydrous potato starch (or preferably, about 3 grms. of air-dried potato starch) is heated with a mixture of about 200 c.c. water and 20 c.c. hydrochloric acid of sp. gr. 1·125 for 3 hours in a boiling water-bath. Under these conditions, 100 parts of starch are said to yield 111·1 parts of glucose, *i.e.*, the maximum quantity theoretically possible. Salomon subsequently observed[9] that if rice starch is used instead of potato starch the maximum yield of glucose is only 106·8 per cent. and he concluded that in the preparation of rice starch industrially, a small proportion of the starch is so altered that complete conversion into sugar

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[1] *Ber.*, 1880, **13**, 1395; 1890, **23**, 3295.

[2] *Ibid.*, 1897, **30**, 2415; 1898, **31**, 1791.

[3] *Chem. Zeit.*, 1907, **31**, 126.

[4] *Compt. rend.*, 1912, **155**, 617.

[5] *Ibid.*, 1925, **181**, 259.

[6] *Helv. Chim. Acta.*, 1926, **9**, 33.

[7] *Schweigg, J.*, 1812, **4**, 108.

[8] *J. pr. Chem.*, 1882, **25**, 348.

[9] *Ibid.*, 1882, **26**, 324.

is no longer possible. It may be, however, that the smaller yield of glucose from rice starch is due, in part at least, to the presence of hemicelluloses in this starch observed by S. B. Schryver and E. M. Thomas.[1]

According to F. Allihn[2] the maximum yield of glucose from starch is obtained by boiling the latter with dilute hydrochloric acid (2 per cent. concentration) for 90 minutes. If more concentrated acid is used, partial decomposition of glucose may occur, and with more dilute acid the period of hydrolysis is unduly prolonged. Although glucose appears to be the sole final product of acid hydrolysis, maltose is certainly formed as an intermediate product and there is no ground for assuming that the acid hydrolysis proceeds differently from diastatic hydrolysis in the earlier stages.[3] According to J. Effront[4] maltose is always formed in the acid hydrolysis of starch, the amount increasing with the progress of saccharification to a certain stage when it attains 34–38 per cent. of the amount of glucose. G. H. Morris[5] proved the presence of maltose in a product of acid hydrolysis by preparing maltosazone therefrom, and Rolfe and Haddock[6] similarly proved the presence of maltose in commercial glucose made from starch by acid hydrolysis. Further, G. Defren[7] succeeded in isolating the actual sugar from the product of the acid hydrolysis of starch.

D. R. Nanji and R. G. L. Beazeley[8] consider that the acid hydrolysis of starch is an extremely involved process, being the resultant of more than a dozen simultaneous reactions Ordinary starch consists, according to them, of the calcium salts of the phosphoric esters of amylose and amylopectin.[9] The liquefaction of starch paste and the conversion of ordinary into soluble starch, either of which processes represents the

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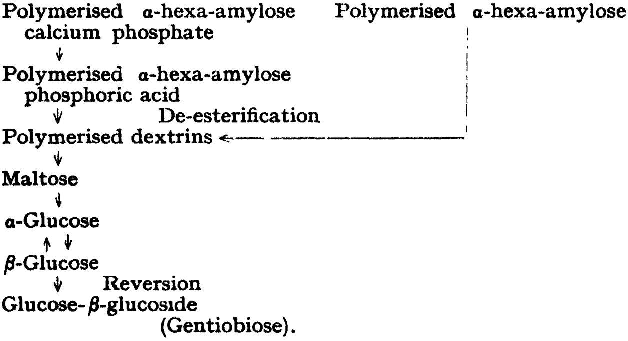
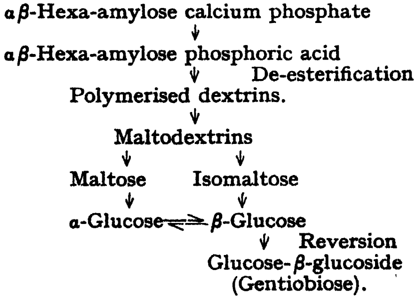
[1] *Biochem. J.*, 1923, **17**, 497.
[2] *Zeitsch. deut. Ver. Rübenzucker*, 1883, 786.
[3] A. Fernbach and M. Schoen, *Bull. Soc. chim.*, 1912, **11**, 303.
[4] *Monit. Scient.*, 1887, 513.
[5] *Proc. Brit. Assoc.*, Sept., 1899.
[6] *J. Amer. Chem. Soc.*, 1903, **25**, 1015.
[7] Eighth Int. Congr. Appl. Chem., 1912, *via*, 111.
[8] *J. Soc. Chem. Ind.*, 1926, **45**, 215T.
[9] See pp. 24–27.

first stage in the acid hydrolysis of starch, is considered to be due to the conversion of these calcium salts into the free phosphoric esters. As evidence of this, Nanji and Beazeley observe that whereas the ash of natural starch contains 25–30 per cent. of calcium and magnesium, soluble starch contains neither element, and that if soluble starch is washed with water containing a trace of calcium salt, it abstracts calcium from the water and, at the same time regains gelatinising power. They also consider that isomaltose,[1] formed directly from the starch, and gentiobiose formed from glucose by reversion, are produced in the course of the acid hydrolysis of starch although they are not formed until 76–82 per cent. of the starch has been hydrolysed to maltose and dextrose. They represent the hydrolysis of amylose and amylopectin—the two constituents of starch—by the following schemes:

HYDROLYSIS OF AMYLOSE BY ACIDS.



HYDROLYSIS OF AMYLOPECTIN BY ACIDS.



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[1] See p. 40.

These schemes do not conflict with the fact that under suitable conditions of acid hydrolysis, a practically quantitative yield of glucose can be obtained from starch since, under such conditions (moderate concentration of acid and minimum heating) there is little or no reversion to gentiobiose. H. Berlin[1] has shown that the mother liquor from the manufacture of glucose contains gentiobiose (see p. 207).

The action of sulphurous acid on starch is much less rapid than that of the stronger mineral acids; according to Bergé[2] the action is very slow below 45°, hydrolysis to glucose beginning at 100° and being complete between 135 and 140° C.

*Enzymic hydrolysis.*—It has long been known that starch paste is readily hydrolysed by aqueous extracts of raw or malted cereal grains; the active principle or enzyme which effects this change was named diastase by Biot and Persoz.[3] Diastase, or amylase as it is sometimes called, is widely occurring in plants and animals and is frequently associated with maltase, the enzyme which hydrolyses maltose to glucose. Diastase occurs in the green foliage leaves of plants and is especially abundant in cereal seeds; it also occurs in the blood, saliva, intestinal and pancreatic juices of animals,[4] and is commonly present in fungi, notably *Aspergillus oryzae* from which the commercial preparation, taka diastase, is made. As to how far diastases from different sources are identical or similar, little definite evidence is yet forthcoming since very little is known of the real nature of diastase or of enzymes in general and no enzyme has yet been prepared in a pure state; indeed the sole criterion of purity of an enzyme preparation is its degree of activity and this only serves for comparison between one preparation and another.

The diastase from malted barley, or malt diastase, has been more thoroughly studied than the enzyme from any other source. It may be obtained by extracting finely ground, pale malt with distilled water for 3–4 hours at room temperature and then filtering. The filtrate (malt extract) may be used

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[1] *J. Amer. Chem. Soc.*, 1926, **48**, 2627.

[2] *Bull. Assoc. Belg.*, 1896–7, **10**, 444.

[3] *Ann. Chim. Phys.*, 1833, **52**, 72.

[4] C. Hamburger, *Pflüger's Archiv.*, 1895, **60**, 543.

directly or the diastase may be precipitated by strong alcohol and dried, in which condition it retains its activity for a considerable period. S. Fränkel and M. Hamburg[1] have described a method of preparing "pure" diastase, but a more practicable method of obtaining a very active diastase is that of H. C. Sherman and A. W. Thomas.[2] One litre of commercial malt extract of high concentration (e.g., sp. gr. 1·27) is divided into 50 c.c. portions each of which is dialysed in a 500 c.c. collodion sac against water at 5–10° C. for 24 hours. The liquors are then decanted or centrifuged from the deposits, the clear solution is placed in an ice-bath, treated with crystallised ammonium sulphate (45 grms. per 100 c.c.) and stirred almost continuously until the crystals have dissolved. The precipitate formed is centrifuged and dissolved in 500–600 c.c. of cold water; the solution thus obtained is dialysed as before for about 20 hours, decanted from any deposit and treated with an equal volume of cold alcohol (99·8 per cent.), the temperature being kept below 15° C.; the precipitate is removed by centrifuging and rejected and enough cold alcohol is added to the liquid to bring the alcohol-content of the whole to 65 per cent. by volume, the precipitate thus obtained being separated by centrifuging and dried in a partial vacuum over sulphuric acid in the dark at a temperature not exceeding 15° C. Sherman and Thomas thus obtained preparations possessing the very high activity of 2150–2350 on the Lintner scale.

Sherman and Schlesinger[3] obtained diastase of yet greater activity from pancreatin powder by the following procedure:—Twenty grms. of pancreatin powder is thoroughly mixed with 200 c.c. of 50 per cent. alcohol at a temperature of 15–20° C., left for 5–10 minutes and filtered through paper, the temperature of the solution not being allowed to exceed 20° C. The filtrate is poured, with stirring, into 7 vols. of a mixture of 1 part alcohol and 4 parts ether. Within 10–15 minutes the precipitate will usually have collected as an oily layer at the

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[1] See *J. Inst. Brew.*, 1906, **12**, 714.
[2] *J. Amer. Chem. Soc.*, 1915, **37**, 643.
[3] *J. Amer. Chem. Soc.*, 1912, **34**, 1104.

bottom of the vessel. The supernatant liquor is decanted and the precipitate dissolved in the minimum amount of water at 10–15 °C. and reprecipitated at once by pouring into 5 vols. of absolute alcohol. The flocculent precipitate is left to settle at a temperature not exceeding 20° C., filtered and dissolved in 200–250 c.c. of 50 per cent. alcohol containing 5 grms. maltose. The solution, which need not be perfectly clear, is next dialysed in a 500 c.c. collodion sac against 2000 c.c. of 50 per cent. alcohol at a temperature of 15–20° C. The dialysate is replaced by an equal volume of 50 per cent. alcohol after 15 hours and again after another 8–9 hours, dialysis being continued for 40–42 hours. The liquid is then filtered and poured into an equal volume of a mixture of equal parts alcohol and ether. The precipitate is filtered in the cold and immediately placed in a vacuum desiccator to dry. The preparation is at least twice as active as that obtained from malt extract. A sample obtained by Sherman and Schlesinger, tested at 40° C., showed the very high activity of 5000–6000 on Lintner's scale; acting at a concentration of 1:100,000,000 on 1 per cent. starch solution, it converted 1,000,000 times its weight of starch to the erythrodextrin stage in 30 hours and in 96 hours it had completely digested the starch and intermediate dextrins to products giving no reaction with iodine and had formed over 500,000 times its weight of reducing sugar calculated as maltose.

Methods of enzyme purification, based on selective adsorption, which were used by Willstätter in the case of invertase, have been successfully applied to the preparation of diastase of very high activity. H. Luers and E. Sellner[1] claim to have thus obtained a malt amylase of about twice the activity of any previously prepared.

The action of diastase on starch comprises two phases, *viz.* liquefaction and saccharification; according to Fränkel and Hamburg[2] a partial separation of malt diastase into liquefying and saccharifying fractions can be effected by dialysis. The view that the diastatic liquefaction and saccharification of

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[1] *Woch. f. Brau.*, 1925, **42**, 97, 103, 110.

[2] See *J. Inst. Brew.*, 1906, **12**, 714.

starch are effected by two enzymes is supported by T. Chrzaszcz and others[1], and also by the observation that they have different temperature optima; whereas the saccharifying power of malt diastase is greatest at 50–55° C., the maximum liquefying power occurs at 60–65° C. at which temperature the saccharifying power is considerably weakened. Taka diastase has very high liquefying power and Sherman and Tanberg,[2] who obtained a very active preparation by extracting commercial taka diastase with water, precipitating with ammonium sulphate, dialysing, and fractionally precipitating with alcohol, found that their product had quite as high a ratio of liquefying to saccharifying power as that of the original material.

Diastatic activity is greatly affected by the reaction of the medium. Most commercial starches, especially rice starch, are slightly alkaline owing to presence of lime and this alkalinity suffices to retard hydrolysis very appreciably, preliminary neutralisation with acid being necessary if maximum saccharification is to be attained. A. Fernbach[3] found that a given quantity of diastase saccharifies the greatest quantity of starch when the medium is neutral to methyl orange, whilst L. Maquenne and E. Roux[4] showed that to effect a maximum conversion of starch into maltose (using an excess of malt extract) the starch paste should be made neutral to methyl orange and the malt extract treated with 30–40 per cent. of the amount of acid necessary to render it neutral to methyl orange. Under these conditions starch is almost completely hydrolysed to maltose although the amylopectin constituent is hydrolysed comparatively slowly. It was subsequently shown by Fernbach and Wolff[5] that neutrality to methyl orange is also the optimum condition for the diastatic liquefaction of starch. These results have been confirmed by

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[1] *Woch. f. Brau.*, 1911, **28**, 510; 1912, **29**, 590; 1913, **30**, 538; *Biochem. Zeitsch.*, 1917, **80**, 211.

[2] *J. Amer. Chem. Soc.*, 1916, **38**, 1638.

[3] *Ann. Brass et Dist.*, 1899, **2**, 409.

[4] *Compt. rend.*, 1906, **142**, 124.

[5] *Ibid.*, 1907, **145**, 261.

Sherman, Thomas and Baldwin,[1] who found that the saccharifying power of malt diastase is greatest at H-ion concentration of $P_H = 4{\cdot}4 - 4{\cdot}5$ (corresponding to $0{\cdot}0006N$ acetic or $0{\cdot}0002N$ hydrochloric acid). Taka diastase is most active at almost the same value, *viz.*, $P_H = 4{\cdot}8$, but pancreatic diastase acts best in a neutral medium, the optimum point being $P_H$ = about 7.

The main product of the diastatic hydrolysis of starch is the sugar, maltose, together with dextrins of various degrees of complexity which are themselves converted into maltose on further diastatic hydrolysis. According to R. Kuhn,[2] taka diastase and pancreatic diastase liberate maltose from starch in its decreasing mutarotatory form, *i.e.* as $\alpha$-maltose, whereas malt diastase liberates it in its increasing mutarotatory form, *i.e.* as $\beta$-maltose Hence, taka and pancreatic diastase attack an $\alpha$-glucosidic linkage of starch whilst malt diastase attacks a $\beta$-glucosidic linkage, and it appears that diastases are divisible into $\alpha$- and $\beta$- groups according to the kind of maltose they produce from starch initially. Taka and pancreatic diastases would thus be $\alpha$-diastases, and malt diastase would be a $\beta$-diastase.

In addition to maltose, formation of glucose sometimes occurs in the diastatic hydrolysis of starch, though the amount is generally small, the quantity produced being no doubt dependent on the proportion or activity of the maltase which is frequently associated with diastase. Thus, C. Hamburger[3] found both diastase and maltase in blood, saliva, intestinal juice and pancreatic juice, and L. Cuisinier[4] observed that certain cereals—especially maize—contain maltase, whilst Sherman and Punnet[5] found that malt, pancreatic and taka diastase all form some glucose from soluble starch, though the amount is small by comparison with that of maltose. The action of maize maltase was investigated by R. Geduld[6] and by C. J. Lintner[7] who noted that if a starch conversion is made into a thin paste with coarsely ground maize and kept

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[1] *J. Amer. Chem. Soc.*, 1919, **41**, 231.

[2] *Annalen.*, 1925, **443**, 1.

[3] *Pflüger's Archiv.*, 1895, **60**, 543.

[4] *Zeitsch. ges. Brauw.*, 1886, **9**, 257.

[5] *J. Amer. Chem. Soc.*, 1916, **38**, 1877.

[6] *Woch. f. Brau.*, 1891, **8**, 545.

[7] *Zeitsch. ges. Brauw.*, 1892, **15**, 123.

at 60° C. for two hours, the whole of the starch is converted into glucose. Z. Wierchowski[1] found that by extracting ground maize with water, the diastase, but not the maltase, is removed, and the extracted maize acts much more vigorously on maltose but much less vigorously on starch than before; the sole product of its action on starch is glucose, no dextrins being formed and even when 80–90 per cent. of the starch has been saccharified the remainder continues to give a blue colour with iodine provided that the ground maize has been completely freed from diastase. Millet and buckwheat also appear to contain relatively large quantities of maltase, and barley, rye, wheat and oats contain small quantities.

H. Pringsheim and J. Leibowitz[2] have pointed out that the combined action of α- and β- diastases on starch (cp. R. Kuhn, p. 63) should yield glucose, and experiments with mixtures of malt and pancreatic diastases appear to bear this out.

## CHEMICAL REACTIONS OF STARCH.

*Chlorine.*—Chlorine appears to have no action on starch in the solid state, but if a current of the gas is passed through a thin paste of starch, the latter is rendered soluble and partly dextrinised.

*Bromine.*—Bromine imparts a yellow colour to starch, but no definite compound appears to be formed.

*Iodine.*—On adding iodine solution to a very dilute solution of starch, an intense blue colour is produced, due to the formation of so-called iodide of starch. If a more concentrated starch solution or if a paste or suspension of starch is used, the iodide is thrown down as a violet or bluish-black precipitate which, when washed and dried, shows a metallic lustre. Starch iodide is also formed when iodine vapour is brought in contact with moist starch, but not if the starch is quite dry.[3] Starch iodide is only very slightly soluble in water; the blue colour disappears when the solution is heated and re-appears on cooling though not so strongly as before.

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[1] *Biochem. Zeitsch.*, 1913, **56**, 209; 1913, **57**, 125.

[2] *Ber.*, 1925, **58**, 1262.

[3] H. B. Stocks, *Chem. News*, 1887, **56**, 212; 1888, **57**, 183.

The extremely delicate reaction between starch and iodine serves as a unique test for both substances. Its application in titrations with iodine is well known, and it has proved of the utmost value for detecting and locating starch in plant tissues. According to E. Chrétien and H. Vandenberghe,[1] 500 c.c. of distilled water, free from ammonia and nitrous acid, containing 0·05 grm. of potassium iodide, free from iodate, and 1 c.c. of 1 per cent. starch paste, gives a distinct blue colour with as little as 0·1 c.c. $N/100$ iodine solution at 10° C.; at 19° and 28° C., 0·15 and 0·25 c.c. are required, and the colour is less distinct. The iodine test also serves as a most useful control of the course of acid or diastatic hydrolysis of starch, since the deep blue colour characteristic of starch and soluble starch changes through violet or purple to reddish brown, and finally to pale yellowish red as hydrolysis progresses.

Despite numerous investigations, opinions are diverse as to the nature and composition of starch iodide. According to F. Mylius,[2] the reaction only occurs when hydriodic acid or an iodide is present besides free iodine and he assigned the formula $(C_{24}H_{40}O_{20}I)_4$ HI to the product. The view that the presence of an iodide is essential was supported by C. F. Roberts[3] who found that if a chloroform solution of iodine is well washed with water to free it from hydriodic acid, and immediately shaken with pure water and starch emulsion, no colour is produced; if, however, a small quantity of hydrochloric acid or potassium iodide is added, or if the liquid is heated or exposed to sunlight, whereby traces of hydriodic acid are formed, the blue colour at once appears. Again, C. Meineke[4] found that an aqueous solution of iodine may be added to a starch solution until the liquid is decidedly yellow without developing any blue colour, and if a trace of potassium iodide is then added, the blue colour is formed. These observations appear to confirm Mylius's view, but further investigation has shown that the blue colour can be obtained in presence of salts other than soluble iodides.

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[1] *Ann. Chim. anal.*, 1921, **3**, 19.
[2] *Ber.*, 1887, **20**, 688.
[3] *Amer. J. Sci.*, 1894, **47** [3], 422.
[4] *Chem. Zeit.*, 1894, **18**, 157.

According to G. Rouvier,[1] starch and iodine form the compounds: $(C_6H_{10}O_5)_{16}I_2$; $(C_6H_{10}O_5)_{16}I_3$; $(C_6H_{10}O_5)_{16}I_4$; $(C_6H_{10}O_5)_{16}I_5$, which are successively produced as the amount of iodine solution added to a given quantity of starch is increased, the intermediate members of the series having the power to dissolve more iodine. According to L. W. Andrews and H. M. Goettsch,[2] starch solution dissolves iodine to such an extent that, after allowing for the iodine taken up by the water alone, the proportion taken up by the starch corresponds to the formula $(C_6H_{10}O_5)_{12}I$, and if starch is heated at 100° C. for a short time with excess iodine so much of the latter is taken up as corresponds with the formula $(C_6H_{10}O_5)_{12}I_2$. H. von Euler and K. Myrback,[3] from measurements of the distribution of iodine between benzene and starch solution, inferred the existence of two compounds of starch and iodine to which they assigned the formulae $(C_6H_{10}O_5)_{18}I_2$ and $(C_6H_{10}O_5)_{18}I_4$.

It has also been held that starch iodide is no definite chemical compound, but a solid solution of iodine in starch,[4] [5] whilst some have maintained that it is an adsorption compound of starch and iodine.[6] [7] [8]

A. Lumière[9] proposed to use starch iodide for disinfecting wounds. Free iodine, in contact with the tissue, soon disappears but starch iodide continues active for a comparatively long period. Starch iodide containing only 1 part iodine in 50,000, suffices to kill *streptococci*, *B. pyocyaneus* and *B. coli* in 24 hours at 37° C., whilst *staphylococci* are still more readily destroyed. Starch can take up 18–20 per cent. of iodine, but starch iodide of this iodine-content is irritant, and an iodine-content of 1 per cent. appears to be generally suitable. Lumière also states that a solution of starch iodide

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[1] *Compt. rend.*, 1892, **114**, 128, 749, 1366; 1893, **117**, 281, 461; 1894, **118**, 732; 1895, **120**, 1179; 1897, **124**, 565.

[2] *J. Amer. Chem. Soc.*, 1902, **24**, 865.

[3] *Annalen*, 1922, **428**, 1; *Arkiv. Kem. Min. Geol.*, 1922, **8**, 1.

[4] F. W. Kuster, *Annalen*, 1894, **283**, 360; *Ber.*, 1895, **28**, 783.

[5] M. Katayama, *Zeitsch. anorg. Chem.*, 1907, **56**, 209.

[6] A. Lottermoser, *Zeitsch. angew. Chem.*, 1921, **34**, 427; 1924, **37**, 84.

[7] L. Berczeller, *Biochem. Zeitsch.*, 1922, **133**, 502.

[8] N. R. Dhar, *J. Physical Chem.*, 1924, **28**, 125.

[9] *Compt. rend.*, 1917, **165**, 376.

containing 0·5 grm. iodine per litre can be used in the irrigation method of treating wounds.

## ACTION OF ACIDS ON STARCH.

Starch is hydrolysed to glucose on heating with dilute acids, but, on treatment with concentrated acids under appropriate conditions, esters are formed in some cases.

*Nitric acid.*—The following nitric esters of starch have been prepared:—

Starch trinitrate, $C_{12}H_{17}O_7(NO_3)_3$, was obtained by H. T. Brown and J. H. Millar[1] by treating 12 grms. soluble starch with 70 c.c. strong nitric acid at 0° C., and precipitating first with 70 c.c. strong sulphuric acid and then with water. On treating the product with dilute ammonium sulphide solution and hydrogen sulphide, soluble starch is regenerated.

Starch tetranitrate, $C_{12}H_{16}O_6(NO_3)_4$, was obtained by Béchamp in two isomeric forms by mixing a fresh cold solution of starch in concentrated nitric acid with sulphuric acid and diluting the mixture with water. The isomers may be separated by alcohol, one of them (ignition point, 178° C.) being soluble and the other (ignition point, 172° C.) insoluble.

Starch pentanitrate, $C_{12}H_{15}O_5(NO_3)_5$, was prepared by Mülhaüser[2] by adding 20 grms. of rice starch (previously dried at 100° C.) in small portions at a time to a mixture of 100 grms. nitric acid (sp. gr. 1·501) and 300 grms. sulphuric acid (sp. gr. 1·8); the whole was left for 1 hour and then poured into a large volume of water, the precipitate obtained being washed and freed from any tetranitrate by treatment with alcohol. The pentanitrate ignites at 160° C.

Starch hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$ was described by W. Will and F. Lenze[3] as an amorphous powder which decomposes at 194° C. without previously melting, but with very explosive violence. According to A. V. Saposchnikoff,[4] the compound has a molecular weight corresponding to the formula, $C_{36}H_{43}O_{13}(NO_3)_{17}$.

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[1] *Chem. Soc. Trans.*, 1899, **75**, 308.

[2] *Ding. Polyt. J.*, 1892, **284**, 137.

[3] *Ber.*, 1898, **31**, 68.

[4] *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 126.

Processes for the manufacture of nitro-starch for use as an explosive have been devised but the product does not appear to have come into general use since it is very hygroscopic and, on account of insufficient purity, it is liable to undergo spontaneous decomposition.

*Sulphuric Acid.*—M. Hönig and S. Schubert[1] obtained sulphuric esters of starch of the general formula $C_{6n}H_{10n}O_{5n-x}(SO_4)_x$, by grinding starch with concentrated sulphuric acid. Amylodisulphuric acid was obtained in the form of its potassium salt, $C_6H_8O_3(SO_4)_2K_2 1/2H_2O$, by R. Tamba[2] by acting on starch with a mixture of chlorosulphonic acid and chloroform in dry pyridine.

*Phosphoric Acid.*—Amylophosphoric acid is formed, according to J. Kerb[3] by treating soluble starch with a solution of phosphoryl chloride in chloroform in presence of calcium carbonate.

*Formic Acid.*—According to J. Traquair,[4] dry starch, on being mixed with 1·5–2 times its weight of 99 per cent. formic acid, swells to a paste in three minutes. If this paste is heated on the water-bath for 15–20 minutes it is converted into a clear gummy solution, and this, on being heated with an equal volume of 90 per cent. formic acid for 5 minutes and then poured into water, yields a plastic mass which dries to a clear, gum-like product. This formic ester is not very stable, slowly losing formic acid in contact with air or water; it is readily hydrolysed by alkali and the regenerated starch gives the usual intense blue colour with iodine. The product obtained by 30 minutes treatment appears to be the monoformate. On more vigorous treatment with formic acid, starch takes up a quantity of acid corresponding to the triformate, but this product does not regenerate starch on hydrolysis.

*Acetic Acid.*—Acetylated starch was prepared by F. Pregl[5] by treating Zulkowski's soluble starch (see p. 56), with acetic anhydride in presence of sulphuric acid; according to the quantity of sulphuric acid in the acetylating mixture, a soluble

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[1] *Monatsh.*, 1885, **6**, 708; 1886, **7**, 455.

[2] *Biochem. Zeitsch.*, 1923, **141**, 274.

[3] *Ibid.*, 1919, **100**, 3.

[4] *J. Soc. Chem. Ind.*, 1909, **28**, 288.

[5] *Monatsh.*, 1901, **22**, 1049.

or an insoluble triacetate is formed. The soluble compound has the composition, $C_6H_7O_5(C_2H_3O)_3$, and its molecular weight has a value eight or nine times that of the empirical formula; its optical activity is $[\alpha]_D = + 163{\cdot}6°$, and on hydrolysis with potassium hydroxide it is stated to yield a soluble starch identical with the original material. The insoluble triacetate (insoluble in alcohol) has the empirical formula, $C_6H_7O_5(C_2H_3O)_3$, and appears to have a molecular formula three times as large; its optical activity is $[\alpha]_D = + 148{\cdot}6°$ and on hydrolysis it yields what appears to be an erythrodextrin.

It is worthy of note that starch is capable of being esterified to the extent of three formyl or acetyl groups per hexose group, and that in the case of one of the triacetates, starch can be regenerated from the product. It is reasonable to assume that these esters correspond in constitution to the trimethyl starch obtained by the exhaustive methylation of starch (see p. 41) as described by Irvine and Macdonald.

C. F. Cross, E. J. Bevan and J. Traquair[1] have obtained technically valuable products by the acetylation of starch. Dry starch is heated with excess of glacial acetic acid (not less than 10 per cent. of the weight of starch) for 8 hours at 90° C., or for 2–3 hours at 120° C. The acetylated product thus obtained is insoluble in cold water but when gelatinised with 5–6 times its weight of boiling water it gives a clear homogeneous solution which does not set or become turbid on standing for a few hours; the solution does not reduce Fehling's solution and it gives the blue reaction with iodine. If a small quantity of the solution is left to dry on a glass plate it forms a clear flexible film. The product is said to be an ideal substitute for gelatin and vegetable gums, and by varying the conditions of manufacture the nature of the product can be altered to suit different requirements. The product is marketed under the name of "Feculose."

*Higher Fatty Acids.*—The acid chlorides of some of the higher fatty acids have been used for preparing the corresponding starch esters. Thus, according to H. Gault,[2] on

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[1] *Chem. Zeit.*, 1905, **29**, 527; *J. Soc. Chem. Ind.*, 1909, **28**, 288.
[2] *Compt. rend.*, 1923, **177**, 592.

heating starch with lauryl chloride in presence of pyridine and with toluene as solvent, starch dilaurate, $C_6H_8O_3(COOC_{11}H_{23})_2$, is obtained in 80 per cent. yield.

By acting on starch with the acid chlorides in quinoline solution, P. Karrer and Z. Zega[1] obtained starch hexapalmitate, $C_{12}H_{14}O_4(COOC_{15}H_{31})_6$, which sinters at 54° C., and melts completely at 75° C., and starch hexastearate, $C_{12}H_{14}O_4(COOC_{17}H_{35})_6$, which sinters at 69° C. and melts completely at 86° C.

C. F. Cross, E. J. Bevan and J. F. Briggs[2] found that by saturating dry starch with carbon disulphide and stirring into the mixture a 15–20 per cent. solution of sodium hydroxide, a reaction occurs which is complete in 2 to 4 hours. The product, dissolved in water, forms a viscous solution of sodium starch xanthogenate and this, on acidification with acetic acid and treatment with iodine solution, yields starch dixanthogenate

as a pulverulent precipitate.

The following alkyl ethers of starch have been prepared:—

*Methylated Starch.*—J. C. Irvine and J. Macdonald,[3] by treating starch with methyl iodide and silver oxide obtained a dimethyl starch of the empirical formula $C_6H_8O_5(CH_3)_2$, and by more drastic methylation with methyl sulphate and alkali hydroxide they obtained first a methyl starch containing seven methyl groups per three hexose groups and finally a trimethyl starch of the empirical formula $C_6H_7O_5(CH_3)_3$. On hydrolysis trimethyl starch yields 2- 3- 6- trimethyl glucose.

*Ethylated Starch.*—L. Lilienfeld[4] prepared ethyl ethers of starch by acting on the latter with ethyl iodide or ethyl sulphate in 10 per cent. solution of sodium hydroxide.

*Allyl Starch.*—C. G. Tomecka and R. Adams[5] prepared

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[1] *Helv. Chim. Acta.*, 1923, **6**, 822.

[2] *Chem. Soc. Trans.*, 1907, **91**, 612.

[3] *J. Soc. Chem. Ind.*, 1922, **41**, 363R; *Chem. Soc. Trans.*, 1923, **123**, 898; 1926, **129**, 1502.

[4] *Chem. Zentr.*, 1921, iv., 40.

[5] *J. Amer. Chem. Soc.*, 1923, **45**, 2698.

allyl starch by treating starch with allyl bromide in presence of a 10 per cent. solution of sodium hydroxide.

*Benzyl Starches.*—M. Gomberg and C. C. Buchler[1] obtained monobenzyl starch $C_{12}H_{19}O_{10}(C_7H_7)$ by the action of benzyl chloride and aqueous sodium hydroxide on potato starch at about 90° C. for several hours. They also obtained dibenzyl starch, $C_{12}H_{18}O_{10}(C_7H_7)_2$, from maize starch by a similar treatment.

*Triphenylmethyl Starch.*—B. Helferich and H. Koester[2] prepared this ether by acting on rice starch with triphenylmethyl chloride and pyridine.

## ACTION OF OXIDISING AGENTS ON STARCH.

*Potassium Permanganate.*—C. J. Lintner[3] found that starch is converted by potassium permanganate into an acid substance of a dextrinous nature.

*Nitric Acid.*—According to O. Sohst and B. Tollens[4] saccharic acid is formed on heating starch with dilute nitric acid.

*Hydrogen Peroxide.*—Z. Gatin-Gruzewska[5] found that hydrogen peroxide hydrolyses and oxidises starch simultaneously, the final products being maltose and oxalic acid.

## ACTION OF LIGHT AND ELECTRICITY ON STARCH.

Starch solutions undergo more or less hydrolysis and decomposition when subjected to high frequency radiation. L. Massol[6] found that if a 0·2–1 per cent. solution of soluble starch is exposed to ultra-violet rays, the iodine reaction undergoes the changes of colour similar to those observed at various stages of starch hydrolysis, and the solution acquires reducing power. H. A. Colwell and S. Russ[7] observed that if a starch solution is exposed for several hours to X-rays of moderate penetrating power, it undergoes a remarkable

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[1] *J. Amer. Chem. Soc.*, 1921, **43**, 1904.

[2] *Ber.*, 1924, **57**, [B], 587.

[3] *Zeitsch. angew. Chem.*, 1890, 546.

[4] *Annalen.*, 1888, **245**, 1.

[5] *Compt. rend.*, 1909, **148**, 578.

[6] *Ibid.*, 1911, **152**, 902.

[7] *Proc. Phys. Soc., London*, 1912, **24**, 217.

decrease of opacity and viscosity and the starch is partly converted into soluble starch and dextrin. E. C. C. Baly and E. S Semmens[1] showed that plane-polarised light strongly accelerates the diastatic hydrolysis of potato, wheat or maize starch. According to W Löb[2] a 1 per cent solution of starch when subjected to the action of a silent electric discharge for 2–3 hours loses the power of giving a reaction with iodine and becomes capable of reducing Fehling's solution.

## ADSORPTIVE POWER OF STARCH

The adsorptive power of starch towards substances in aqueous solution has been examined by H. Lloyd[3] and by A. W. Rakowski[4] who found that inorganic and organic acids and salts are not adsorbed or only slightly adsorbed. Alkalis, hydroxides of heavy metals in ammoniacal solution and basic colouring matters are markedly adsorbed by starch.

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[1] *Proc. Roy. Soc.*, 1924, **B97**, 250.

[2] *Biochem. Zeitsch.*, 1912, **46**, 121.

[3] *J. Amer. Chem. Soc.*, 1911, **33**, 1213.

[4] *J. Russ, Phys. Chem. Soc.*, 1912, **44**, 586.

# CHAPTER V.

## MICROSCOPY OF STARCH.

For the microscopical examination of starch, a microscope provided with a low power objective (from 1 to ½ inch) for preliminary examination and a fairly high power objective (⅙ inch) for detailed examination is required. A micrometer eyepiece for measuring the granules, polarising and analysing Nicol prisms and a selenite plate for examining the granules with polarised light are also needed.

The operation of mounting the starch for examination is very simple. A small drop of water is placed on a microscope slide and a small quantity of the sample is transferred on the point of a knife to the drop and thoroughly mixed by means of a mounted needle; the drop is then covered with a cover glass and is ready for observation. In placing the cover glass in position, any excessive pressure must be avoided since this might crush the granules. The quantity of starch taken should be such that whilst the field of view shows numerous granules, these should not be so crowded as to overlap since this would interfere both with observation and with measurement. For examination by polarised light, the sample should be mounted in dilute glycerol or Canada balsam. The following characteristics should be observed:—

(1) The size of the granules, (2) The nature of the compound granules if these are present. (3) The shape of the granules. (4) The position and appearance of the hilum or organic centre of the granule. (5) The striae or markings round the hilum. (6) Appearance of the granules in polarised light.

(1) *Size of Granules.*—In determining the size of starch granules it is usual to measure the longer diameter though the shorter diameter is sometimes noted also, and to express the dimensions in microns (1 micron, $\mu$ = 1/1000 millimetre).

The size varies between very wide limits, ranging from a diameter of 1$\mu$ or less to one of 150$\mu$, and whilst in some starches the granules are nearly all large (e.g., canna), and in others nearly all small (e.g. rice), there are yet other starches consisting of both large and small granules. Measurements should be made of the largest and smallest granules and especially of those of the most frequently occurring size.

(2) *Compound Granules.*—Starch may consist of simple granules or of aggregates of granules sometimes called compound granules, or of both kinds. Compound granules are of two sorts, viz. true compound granules consisting merely of an aggregation of component simple granules each with its own hilum and system of concentric striae or markings, and semi-compound granules in which the component granules are surrounded by one or more layers of starch as indicated by striae; semi-compound granules are not of very frequent occurrence.

Compound granules may consist of from two to several hundreds of component granules and they are frequently more or less broken up into their component granules in the process of extracting the starch from the plant organ so that compound granules are more abundant in the undisturbed starch of the plant than in manufactured starches. The separated component granules from compound granules are often indistinguishable from simple granules of the same starch, though their shape (see below) sometimes indicates their origin.

(3) *The shape of the Granules.*—No scheme of classification of starches, according to the shape of the granules, can be altogether free from objection, since the granules of most starches exhibit considerable diversity of form, and some granules also are of shapes intermediate between two types e.g. partly globular and partly polygonal. The following classes may be distinguished:—

I Round; II Lenticular; III Elliptical; IV Oval or ovate; V Truncated ; VI Polygonal.

When viewed in certain positions some granules may appear to be round although their actual shape may be different, e.g. lenticular or elliptical. This difficulty may be easily overcome by imparting to the granules, whilst under observation, a slight rotational movement; this is effected either by lightly touching the edge of the cover glass with a needle, or by touching the liquid at one side of the cover glass with a strip of filter paper or by bringing a drop of alcohol to one edge of the cover glass. Truncated, or kettle-drum shaped granules are the separated component granules of compound granules consisting of two components the flat end representing the surface of contact of the granule with its twin in the compound granule. Similarly, components derived from a three-membered compound granule may exhibit two flat surfaces, and the components from larger aggregates have a polygonal shape; the marginal components from large aggregates may have one or two curved sides. In examining the shapes of the granules of a starch it must be remembered that some of the granules may appear quite exceptional in shape for the starch in question, and that the starch is indicated rather by the shape of the *majority* of its granules.

(4) *Position and Appearance of the Hilum.*—The hilum or nucleus is the organic centre round which the granule has grown. It may be placed centrically or excentrically and in the latter case the excentricity or ratio of the shortest to the longest distance of the hilum from the edge of the granule is of some value for identification purposes since it differs widely with different starches. The hilum is conspicuous in the granules of some starches and hardly discernible in others; in some starches it is very small and in others of considerable size. It appears to contain more water and to be softer than the surrounding portions of the granule; and, as a result of drying, the hilum may become cracked or starred with fissures, the nature of this fissuring varying with different starches.

✓(5) *The Striae or Markings.*—The granules of many starches exhibit a series of striae or markings disposed concentrically around the hilum. Some starches (e.g. potato) are distinguished by very pronounced striae, others show only very faint striae whilst others do not appear to be striated at all, although it is most probable, judging from the optical behaviour of starch granules, that all of them possess that stratified structure of which the striae are indicative. It has been suggested that the strata or layers of the granule differ in respect of moisture-content, dense strata of low water-content alternating with softer strata of high water-content; the hilum generally corresponds with the softer, rarely with the denser strata.

The striae are best seen with oblique illumination, and may be rendered more distinct by treating the granules with dilute chromic acid solution. Careful focussing is requisite to render them visible in any individual granule, and of a number of granules in the field of the microscope only a very few will exhibit the striae simultaneously.

(6) *Behaviour in Polarised Light.*—Starch granules observed between the crossed Nicol prisms of a polarisation microscope appear brightly illuminated against the dark background and exhibit a black cross; the point of intersection of the arms of the cross coincides with the position of the hilum and is a useful aid in locating the hilum when this is not otherwise easily seen. If the hilum is centric, the cross is **X**-shaped, if highly excentric, the cross is **V**-shaped. With some starches the cross is very distinct, with others, much less so. If a selenite plate is interposed, a striking play of colours is obtained with many starches.

The cross appears to be due to pressure within the stratified structure of the granule. W. Harrison[1] has pointed out that the cross is rendered more distinct on moistening the dry granule and that the granule swells to a slight extent when moistened. Since the granule is surrounded by a resistant outer coating (amylopectin) any swelling of the interior will increase the internal pressure and thus tend to enhance the intensity of the cross markings. When the outer coating is broken by grinding the granules, the internal pressure is released and this accords with the observation that the crosses disappear as a result of this treatment.

In the actual examination of a starch with a view to its

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[1] *J. Soc. Dyers and Col.*, 1916, **32**, 40.

identification, it must be remembered that although much help is afforded by verbal description and pictorial or photographic representation neither aid is so satisfactory as comparison with known starches. It is very advisable, therefore, to make a collection of samples of as many different kinds of starch as possible. Then, having narrowed the field of inquiry by a preliminary examination of the sample of starch in question, its identity may be finally settled by comparison with samples of known species. The preparation of known starches for the purpose of such comparison is not difficult and may be conveniently effected as follows:—The seed or other plant material from which the starch is to be extracted is ground to a coarse powder, an ordinary coffee mill serving very well for this purpose. The powdered material is sifted through a fine sieve (a 90-mesh sieve is suitable) whereby the finer portion, which contains nearly all the starch, is separated from husk, etc., and from much of the albuminoid matter which being of rather tough consistency does not grind to so fine a powder. The sifted portion is mixed with water to form a thin suspension and the mixture after being thoroughly shaken, is allowed to stand in a tall cylinder for some time. In some cases the starch settles to the bottom of the cylinder in a well-defined white layer from which the supernatant liquor, containing the albuminoid matter in suspension, can be decanted, and the starch may then be purified by repeated washing with water and decantation If the albuminoid matter, etc., forms fairly large flocks, the starch may be separated therefrom very expeditiously by pouring the aqueous suspension on a 90-mesh sieve; if the liquor is kept well stirred, the milky suspension of the starch passes rapidly through the sieve whilst most of the albumin remains as a slimy deposit; the starch thus obtained must of course be further purified by washing and decantation. If it is not found practicable to effect the separation of the starch from albumin, etc., by sedimenting or sifting the aqueous suspension, the latter may be treated with sodium hydroxide solution in such quantity that the concentration does not exceed 0·1 per cent. in the mixture. This treatment causes flocculation of the albumin which can then be removed either by decantation or sieving; the starch should not be left in contact with the alkaline solution longer than necessary. The progress of purification of the starch at each stage can be easily followed by microscopic examination of a mixture of a drop of a suspension of the material and a drop of iodine solution; the starch granules present a bluish-black appearance whereas any albuminoid or other impurity appears yellow or colourless. The purified starch is finally allowed to dry in the air.

The microscopic characteristics of a number of the more important starches are appended and these are followed by brief descriptions of some starches of minor economic importance. The authorities for most of the data given are J. von Wiesner,[1] H. G. Greenish and G. Collin,[2] F Hess,[3] T E. Wallis,[4] and P. Wiegleb.[5]

### ✓WHEAT STARCH (see Figure 25)

Wheat starch consists chiefly of large lenticular granules and small round, or, less often, polygonal ones. Compound granules consist of 2–25 component granules; they are true compound granules and are easily separated into their components. Compound granules of 2 or 3 components occur not infrequently in commercial wheat starches, but higher compound granules become more or less completely broken up in the course of manufacture. The dimensions of the starch granules from different varieties of wheat are shown in Table IV.

It will be noticed that the dimensions of all these starches, excepting that from *Triticum monococcum*, are substantially the same. According to Greenish and Collin the large granules of wheat starch have an average size of 25 to 35$\mu$ and may attain as much as 45$\mu$. T. E. Wallis[6] found that the proportion of granules exceeding 40$\mu$ in wheat starch is only one in five or six thousand.

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[1] *Rohstoffe des Pflanzenreiches*, 3rd ed., Vol. II.

[2] *Pharm. J.*, 1901, **12**, 290, 424, 590.

[3] *Zeitsch. Oesterr. Apoth.-Ver.*, **44**, 25; *Pharm. J.*, 1906, **22**, 129.

[4] *Pharm. J.*, 1923, **56**, 235.

[5] *Zeitsch. Spiritusind.*, 1925, **48**, 370.

[6] *Pharm. J.*, 1922, **55**, 82.

The components derived from the compound granules have the dimensions of the small simple granules excepting in the case of those derived from twins which are generally larger.

The hilum is centric; the striae are indistinct in the large granules and cannot be seen at all in the small granules.

TABLE IV.

| Variety of wheat. | Large granules. | | Small granules. | |
|---|---|---|---|---|
| | Limits of size. | Most usual size. | Limits of size. | Most usual size. |
| Triticum vulgare .. | 14–39μ | 28·2μ | 2·2–8·2μ | 7·2μ |
| ,, durum .. | 11–36μ | 26·1μ | 2·2–7·8μ | 7·2μ |
| ,, turgidum .. | 17·6–41·1μ | 29·0μ | 2·2–8·2μ | 7·2μ |
| ,, spelta .. | 15·4–39·6μ | 27·0μ | 2·5–7·9μ | 7·0μ |
| ,, dicoccum .. | 11·1–30·1μ | 25·9μ | 1·8–6·8μ | 6·6μ |
| ,, monococcum | 12·0–27μ | 19·5μ | 1·8–6·0μ | 5·8μ |

## RYE STARCH (see Figure 24).

Rye starch consists of large and small granules and some of intermediate size. The large granules have an average diameter of about 40μ and may attain 50μ; they are of discoid shape and often exhibit irregular protuberances. The hilum is stellate with concentric striae. The small granules and those of intermediate size include some of hat- and bell-shaped appearance.

Rye and wheat starches are very much alike in appearance; according to W. Lenz[1] they may be distinguished by the following method:—A small quantity of the starch is mixed with water and a thin film of the mixture is placed on a cover glass and allowed to dry. The dried film is treated with a drop of a solution of 1 part of sodium salicylate in 11 parts of water; the edge of the cover glass is touched with vaseline and the glass is mounted on a hollow slide. The starch is microscopically examined at intervals. After 10 or 15 minutes,

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[1] *Int. Congr. Appl. Chem., London,* 1909.

rye starch granules begin to swell and after an hour most of the larger granules are swollen, have a flattened appearance, and no longer show a cross with polarised light. In the case of wheat starch, very few of the granules are affected in the course of an hour, and those which have swollen still retain an appearance of solidity. After longer intervals up to a week, similar differences between the two starches are observable.

### BARLEY STARCH (see Figure 23).

Barley starch, like wheat and rye starches, consists chiefly of large and small granules with a few of intermediate size. The large granules are rather smaller than those of wheat starch and less regular in outline and they are elliptical, reniform, bulb- or pear-shaped, of diameter ranging from 20 to 35$\mu$. They have no apparent hilum, but some show striae; they are rarely fissured and the fissures are much less conspicuous than in rye and never stellate. The granules of intermediate size range from 10 to 15$\mu$ and the small granules are of about the same size as those of wheat and rye starches.

### OAT STARCH (see Figure 30).

Oat starch consists of simple and compound granules. The former average about 10$\mu$ in diameter and most of them are rounded, very few being angular though some are spindle- or lemon-shaped. The compound granules are rounded or oval and range from 35 to 50$\mu$ in length; they may consist of from 5 to 200 components, the inner ones of which are polygonal, whilst the peripheral components are curved on one side and angular on the other; the component granules are generally rather smaller than the simple granules.

According to T. J. Ward,[1] simple granules of much larger size than the average, viz., about 25–30$\mu$ in diameter, are present in small numbers in oat starch. These granules are of rounded shape and their proportion, compared with the numbers of other granules, appears to be about 1 to 300 or 500.

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[1] Private communication.

## RICE STARCH (see Figure 32).

Rice starch occurs in the rice grain both as simple and as compound granules; the latter are egg-shaped, 18–36$\mu$ in diameter (most frequently about 22$\mu$), and consist of 2–100 component granules which are mostly polygonal though those on the outside of the aggregate may have one side slightly rounded. The component granules measure 3–7$\mu$ and generally about 5$\mu$, and are similar in every way to the simple granules. Compound granules are not found in commercial rice starch as they always become broken in the course of manufacture, and the components cannot be distinguished from the simple granules of the original rice grain.

The hilum is centric but not always evident. Striae are not visible directly but may be made so by treatment with dilute chromic acid. The polarisation crosses are distinct, but no play of colour is exhibited with the selenite plate.

Rice starch rather closely resembles oat starch, but the granules are uniformly somewhat smaller and never spindle- or lemon-shaped.

## MAIZE STARCH (see Figure 22).

Maize starch granules show some differences in shape according as they are derived from the mealy interior of the endosperm or from the horny periphery. The horny part contains polygonal granules only, having a diameter of 14–15$\mu$ and sometimes attaining 25 or 26$\mu$. The granules from the interior are rounded or at least not markedly angular, and measure 10 to 25$\mu$ with an average of 13 to 15$\mu$. The mealy interior also contains compound granules which comprise from 2 to 11 components; in the manufactured starch the granules are practically all simple and of polygonal or roundish shape.

In fresh tissues of the plant, the starch granules exhibit a large roundish hilum which, in the dry granule is replaced by a hollow cavity from which fissures radiate.

Striae have not been observed with certainty. The polarisation crosses are distinct.

### Pea Starch (see Figure 11).

Pea starch, obtained from *Pisum sativum* consists of simple granules of reniform or irregularly rounded or oval shape. The size of the granules ranges from about 30 to 40μ, the hilum is frequently fissured but striae are not distinct.

### Lentil Starch (see Figure 12).

Lentil starch, obtained from *Lens esculenta,* consists of simple granules of reniform, rounded or oval shape, and measuring about 20 to 40μ. The hilum is generally fissured, the fissure often being extremely distinct; striae are not easily seen.

### Broad Bean Starch (see Figure 13).

Broad bean starch, from *Vicia faba,* consists of simple granules of reniform, rounded or oval shape, measuring about 20 to 40μ. The hilum is centric and sometimes fissured; striae are perceptible but not distinctly so.

### French Bean Starch (see Figure 9).

French bean starch, from *Phaseolus vulgaris,* consists of simple granules of rounded or oval shape and measuring from about 30 to 50μ. The hilum is centric and generally fissured; the striae are fairly easily seen.

### Scarlet Runner Bean Starch (see Figure 15).

Scarlet runner bean starch, from *Phaseolus multiflorus,* consists of simple granules of rounded or oval shape and measuring from about 20 to 35μ. The hilum is centric and generally radially fissured. Striae are not distinct.

*Note.*—The preceding five leguminous starches are rather similar in appearance. Points especially worthy of note are the marked difference in size between French bean and scarlet runner bean starches and the appearance of pea starch granules resembling potato tubers.

### White Guinea Corn Millet Starch (see Figure 18).

Millet starch from Nigerian White Guinea corn, a variety of *Sorghum vulgare,* consists of rounded polygonal granules of about 15–35μ diameter. The hilum is centric and fissured the fissuring frequently being stellate. Striae do not appear distinguishable.

### DURA, DURRA, OR DHURRA MILLET STARCH (see Figure 19).

Dura, Durra or Dhurra millet starch, from a Sudanese variety of *Sorghum vulgare,* is practically identical in microscopical appearance with the preceding starch.

The seeds of other varieties of *Sorghum vulgare,* viz. *S. vulgare Dura var. Fatarita, S. vulgare Intama* from Tanganyika Territory, and Indian Jowar millet also yield starches practically identical in appearance with Dura millet or White Guinea corn millet starch.

### BULRUSH MILLET STARCH (see Figure 26).

Bulrush millet starch, from a Nigerian variety of *Pennisetum typhoideum,* consists of irregular or rounded polygonal granules of from about 8 to 25μ in diameter. The hilum is centric and sometimes fissured; striae are not visible. Seeds of Indian and Sudanese varieties of *Pennisetum typhoideum* yield starches very similar in appearance to Bulrush millet starch.

### SHAMA MILLET STARCH (see Figure 27).

Shama millet starch from *Panicum colonum* (India) consists of polygonal or rounded polygonal granules measuring from about 8 to 15 or 20μ in diameter. The hilum is centric and generally punctiform, though sometimes slightly fissured; striae are not visible.

### ITALIAN MILLET STARCH (see Figure 28).

Italian millet starch from *Setaria italica* (India) consists of rounded or polygonal granules of about 8 to 15μ in diameter. The hilum is centric and fairly distinct and sometimes slightly fissured; striae are not visible.

### RAGI MILLET STARCH (see Figure 29).

Ragi millet starch, from an Indian variety of *Eleusine coracana,* consists of polygonal granules of about 6 to 20μ in diameter. The hilum is centric and sometimes faintly fissured; striae are not visible.

The seeds of two other varieties of *Eleusine coracana*, viz. Black Wimbi and Red Wimbi seeds, yield starches very similar to Ragi millet starch in microscopic appearance.

### SAGO STARCH (see Figures 4 and 5).

The sago starch of European commerce appears to be manufactured chiefly from *Metroxylon Rumphii* and *Metroxylon laeve*. In the plants the starch occurs in the form of true compound granules but the manufactured starch contains only a comparatively small proportion of unbroken compound granules. The compound granules have a remarkable appearance, consisting, as they do usually, of one large component to which 1–3 small components are attached. The large component may be conical, and frequently has one or two projections to the flat ends of which the smaller granules have been attached. The large components measure 50–65$\mu$ and the small ones from 10 to 20$\mu$.

The hilum is very distinct and fissured and the striae are usually distinct.

Sago or pearl sago, which is prepared from sago starch by heating the latter in the moist state, shows evidence of the treatment to which it has been subjected. Some of the granules retain the characteristic forms of sago starch and can easily be identified whilst others are more or less altered, some exhibiting a gelatinised interior and some being swollen to an unrecognisable mass.

The starch of the roots of the South Asiatic palm, *Borassus flabelliformis*, is also used in India for the manufacture of sago. The starch forms a yellow powder. Most of the granules are simple. The compound granules, like those of the preceding kind, consist of several components of which one far exceeds the others in size. The small granules are spherical whilst the large components of the compound granules are elliptical or bean-shaped and frequently exhibit irregular projections. The length of the granules ranges from 24 to 41$\mu$ and breadth from 14 to 27$\mu$. The hilum is large and, in glycerol, is distinctly visible as a dark body; it is usually radially fissured. The striae are just perceptible, though in a few granules they are somewhat more distinct.

### ARUM STARCH.

This starch, obtained from *Arum esculentum*, consists of compound granules which contain 2–10 components of unequal size and irregular arrangement. The size of the component granules ranges from 3 to 27μ and most frequently between 13 and 20μ. The compound granules do not occur in considerable numbers in the commercial starch. The hilum is always well developed, and is generally marked by radial fissures. Striae are either invisible or indistinct.

### FRITILLARIA STARCH.

This starch consists chiefly of simple granules with occasional small compound granules which comprise 2–3 components and seldom more. The simple granules may be arranged in four groups which are connected by transitional forms. (*a*) Mussel-shaped granules with hilum at the pointed end. (*b*) Oval, triangular or rounded-triangular granules with hilum at the narrow end. (*c*) Bean-shaped granules with hilum at the concave side. (*d*) Small, spherical, concentrically built granules. The length of the mussel- and bean-shaped granules ranges from 32 to 71μ and the breadth from 27 to 55μ; the diameter of the spherical granules ranges from 9 to 17μ.

### MARANTA STARCH (see Figure 10).

Maranta starch, obtained from the rhizomes of *Maranta arundinacea* and other *Maranta* species is the original arrowroot starch and is now known variously as West Indian, Jamaica, Bermuda, St. Vincent and Natal arrowroot to distinguish it from other starches, also called arrowroot. The granules are always simple and similar to those of potato starch in shape but rather smaller, their length ranging between 13 and 70μ and mostly between 27 and 54μ. The hilum may be centric but is more often excentric and it is frequently marked by a fissure in the form of a double curve resembling the wings of a hovering seagull. The striation is always visible, but never strongly marked.

It has been observed[1] that genuine arrowroot starches, prepared from the rhizomes of *Maranta arundinacea* in different parts of the world may be distinguished by their behaviour towards potassium hydroxide solution although their appearance under the microscope is identical. The test, which has been applied to Bermuda, St. Vincent and Natal arrowroots, is carried out as follows:—About 0·5 grm. of the powdered starch is shaken thoroughly with about 20 c.c. of water in a test-tube. The contents of the tube are then poured into a small beaker containing about 50 c.c. of a 2 per cent. solution of potassium hydroxide; the mixture is stirred and left to stand for 5–10 minutes. In the case of Bermuda arrowroot, the starch is gelatinised, a nearly clear, faint blue liquid is produced and there is no deposit. St. Vincent arrowroot is not gelatinised, but a white deposit of swollen granules is obtained. Natal arrowroot is partly gelatinised and gradually settles to the bottom of the beaker as a semi-transparent, gelatinous mass leaving a clear watery liquid above it. It is pointed out that these differences may be due to different methods of preparation of the arrowroots in the countries of origin and further experience is requisite to determine if the test is of permanent value.

According to P. Wiegleb, the starch from *Maranta nobilis* is not so white as ordinary Maranta starch. The granules are mostly simple, 11 to 34$\mu$ long, with centric hilum and only exhibit striae distinctly after treatment with chromic acid which also produces radial fissuring. Compound granules are also observed, but only rarely. They are only about half the size of the simple granules and consist of 2–5 components.

### CURCUMA STARCH (see Figure 7).

Curcuma starch or Travancore starch or East Indian arrowroot is obtained from the rhizomes of *Curcuma angustifolia*, *C. leucorrhiza* and other species of *Curcuma*. The

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[1] *Bull. Imp. Inst.*, 1912, **10**, 566.

granules may be oval, elliptical, almost rectangular or rounded in outline; they are so thin that when viewed on edge they appear very narrow and sometimes several adhere by their flat sides. The granules of the starch from C. *angustifolia* are at most 70μ long and usually about 30–60μ, but those from C. *leucorrhiza* may attain a length of 145μ and are most commonly about 105μ long. The hilum is punctiform and very excentric. The striae are very distinctly marked.

### CANNA STARCH (see Figure 1).

Canna or Tous-les-mois starch or Queensland arrowroot is obtained from the rhizomes of *Canna edulis*, *Canna coccinea* and other species of *Canna*. Some of the granules of this starch are so large that they are visible to the naked eye. The granules are simple and elliptical, oval, oyster-like or reniform in shape; the diameter may range from 10 to 130μ, the most frequent size being about 60μ.

The hilum is rounded and excentric; the striae and polarisation cross are very distinct.

### TACCA STARCH (See Figure 14).

Tacca starch or Tahiti arrowroot or Williams arrowroot, is made from the tubers of *Tacca pinnatifida* and *T. Oceanica*, and consists of both simple and compound granules, but chiefly the latter. The simple granules may be elliptical or egg- or pear-shaped and both simple and component granules are mostly about 25μ in diameter though the largest simple granules may attain 45μ. The hilum is distinct and centric or only slightly excentric. The striae are distinct and the polarisation cross well marked.

### YAM OR DIOSCOREA STARCH.

Yam or Dioscorea starch, or British Guiana arrowroot is made from the tuberous roots of various species of *Dioscorea*.

White Dioscorea starch prepared from *Dioscorea alata*, is a greyish yellow powder It consists of simple granules of irregular, oval or elliptical or rounded triangular contour; the larger extremity of the granule is often truncated. The larger granules measure 45–90$\mu$ long by 25–60$\mu$ broad, whilst the smaller range from 15 to 30$\mu$ long and have about half this breadth. The hilum is distinct and has an excentricity of 1/5–1/7. The striae are distinct and are rendered still more so by chromic acid. The polarisation cross is well marked.

Red Dioscorea starch (*Igname indien rouge*) forms a dirty reddish powder. A small part of the red colour can be washed out with water, but the whole of it cannot be removed even with alcohol. The carriers of this colouring matter are small fragments of parenchymatous tissue, the cells of which are packed with starch granules. The granules themselves, however, are coloured red, and it may be conjectured that they mechanically absorb the colouring matter from the cell juice; the colour is turned bright red by acid, and blue by alkali. The granules resemble those of white Dioscorea starch in form, and striation, though they are somewhat narrower, and range from 17 to 119$\mu$ in length; they also resemble white Dioscorea starch in respect of hilum and polarisation cross.

Yellow Dioscorea starch (*Igname indien jaune*) is a fairly intense greyish yellow to brownish flour. It contains starch-bearing fragments of tissue which frequently have a diameter of 800$\mu$ and are distinguishable by the naked eye. The granules are strikingly unlike those of the white and red Dioscorea starches; they may be elliptical, or egg-, pear-, or heart-shaped, but do not present a truncated appearance; they range from 8 to 55$\mu$ in length. The hilum is not easily distinguished; it appears as a dark spot if the starch is examined in glycerol. The very numerous striae are not so distinct as those of the white and red Dioscorea starches; they become more distinct on treatment with chromic acid.

The granules of the Dioscorea starches are often covered with mould mycelia owing, no doubt, to the fact that these starches are very crude products, containing foreign matter favourable to the growth of micro-organisms.

### Manioc or Cassava Starch (see Figures 16 and 17).

Manioc or Cassava starch, or Brazilian, Bahia, Rio or Para arrowroot is prepared from the tubers of *Manihot utilissima*. The granules are compound, consisting generally of two, but sometimes of three to eight components; most of them become broken up in the course of manufacture of the starch, and most of the components exhibit one or two flat surfaces. The largest components measure 25–35μ and the smallest 5–15μ, many ranging from 15 to 25μ. The granules may be cap-shaped or conical, curved on one side and irregular on the other, and some are polygonal. Most of the granules show a distinct excentric hilum and striae.

Tapioca is prepared by heating cassava starch in a moist state. Many of the granules retain their original shape, some exhibit a translucent interior, and some appear swollen to a shapeless mass.

### Batata Starch.

Batata starch, like the preceding, also known as Brazilian arrowroot, is prepared from *Ipomoea batatas*. It consists chiefly of the separated components of compound granules but still contains some of the latter which may comprise 2–12 components (generally 4 or 5); the starch also contains a very small proportion of simple granules. The component granules are often hemispherical; they vary greatly in size which ranges from 10 to 50μ in diameter, and they exhibit a distinct excentric hilum and well-marked striae. The simple granules have a diameter of 8–25μ and possess a centric or slightly excentric hilum. The striae are distinct and the polarisation cross may be seen with strong magnification, but is never very clearly defined.

### Zamia Starch (see Figure 8).

*Zamia floridana* (de Candolle).—The starch obtained from the tuberous stems of this plant is known as Florida arrowroot and appears to be of considerable economic importance in Florida where the plant occurs. Most of the granules are compound, consisting of 2–8 components and in many cases of three components arranged in a row. In the commercial products most of the compound granules are broken up, the separated components being in many cases hemispherical or dome-shaped, whilst some exhibit large flat faces and slightly rounded ends, these being the middle components from rows of three. The size of the granules varies between very wide limits ranging from about 5 to 75μ. In the fresh starch the hilum is not well marked, and striae are rarely visible, but in the commercial starch, both hilum and striae are generally distinct and radial fissures are also present. The polarisation cross is very distinct. The commercial starch contains clusters of crystals of calcium oxalate ranging from 14 to 60μ in diameter; the presence of these is a valuable aid in identifying the starch.

### Banana Starch (see Figure 6).

Banana starch is prepared from the green fruit or pericarp of *Musa paradisiaca*. The granules are simple and vary from round to rod-shaped in form, the ratio of length to breadth ranging from 1:1 to 6:1; the thickness is small as the granules are flattened or discoid. The longest diameter of the granules ranges from 7 to 58μ and most often between 24 and 48μ. The hilum is always distinctly perceptible and very excentric, and the striae are always very well marked; polarisation cross is very distinct.

### Buckwheat Starch (see Figure 31).

Buckwheat starch, prepared from *Polygonum fagopyrum* consists chiefly of simple polygonal granules which somewhat resemble rice starch granules though rather larger, being of 4–15μ diameter and mostly about 9μ. This starch also contains some very characteristic compound granules consisting of 2–9 components. The latter differ from the simple granules in frequently being somewhat rounded.

### Potato Starch (see Figures 2 and 3).

Potato starch is prepared from the tubers of *Solanum tuberosum*. It consists almost entirely of simple granules and though it also contains twin and triplet compound granules, these are rare and seldom observed. Most of the compound granules are true compound ones but semi-compound ones are occasionally met with. The size of the granules varies very widely, ranging from 15 to 100$\mu$. The large granules (say from 60–100$\mu$) represent the completely mature stage of growth and are distinguished by numerous, well-marked striae of which a few are especially conspicuous; they may be egg- or oyster-shaped, and exhibit a punctiform, excentric hilum at the small end of the granule. The polarisation cross is distinct. The small granules represent earlier stages of development, and, unlike the mature granules, they are only faintly striated or not striated at all; they are round or elliptical in shape.

Saare has classified grades of potato starch according to the average size of the granules (see p. 137). The finer grades of commercial potato starch consist of larger granules than do those of lower quality.

### CHESTNUT STARCH.

Chestnut starch, prepared from the edible nut of *Castanea vulgaris* consists of very variously shaped simple granules together with occasional twin and triplet granules. The simple granules range in size from 1·5 to 30$\mu$ in diameter, most being near the upper or lower limit with only a small proportion of granules of intermediate size. The large granules are generally three- or four-sided, but some are heart- or kidney-shaped or club-shaped.

The small granules are rounded or egg- or pear-shaped. The hilum cannot be seen directly and striae are not visible.

### HORSECHESTNUT STARCH (see Figure 20).

Horsechestnut starch is prepared from the nuts of *Aesculus hippocastaneum.* It consists of both simple and compound granules and a distinction can be made between large and small granules. The small granules measure from 3 to 8$\mu$ in diameter; by far the most of them are simple, and those that are compound consist of equally large components. The large granules measure 14 to 35μ in diameter; they may be either simple or compound, and in the latter case, they comprise, like the granules of sago starch, one large and one or two small granules. The structure of the granules may be so blurred that the compound nature can only be demonstrated with the polarisation microscope. The small simple granules are round or elliptical and are generally concentrically striated. The large granules may be pear-shaped or conical, or very irregular in shape especially if the small components appear as protuberances; the striation of the large granules is distinct and excentric.

### ACORN STARCH (see Figure 21).

Acorn starch consists of simple and compound granules and the separated components of the latter frequently exhibit the hemispherical or kettledrum shape characteristic of the components of two-membered compound granules. The size of the granules ranges from about 5 to 15 or 20μ.

The starches obtained from the following plants are of minor economic importance:—

*Alocasia macrorhiza.*—Granules both simple and compound, the former being 9–45μ long and having a centric hilum. The compound granules consist of 2–3 components.

*Amorphophallus Rivieri.*—The granules are compound, and measure 3·9–6·5μ, the component granules being very minute.

*Artocarpus incisa* (bread-fruit tree).—The starch has a yellowish tinge. The granules are all compound and consist of 2–20 components which are curved at the free surfaces and polygonal elsewhere. The components range in size from 2·5 to 13μ. No hilum or striae are perceptible, and the polarisation cross is only seen under strong magnification.

*Caryota urens.*—The granules are mostly simple, measuring 8–139μ long by 4·5 to 63μ broad; they are elongated, cylindrical or pear-shaped. The hilum and striae are distinctly visible.

*Castanospermum australe.*—The spherical or oval granules of this starch consist of 2–8 components of size ranging from 3 to 15μ. The hilum is distinct, but no striae can be seen

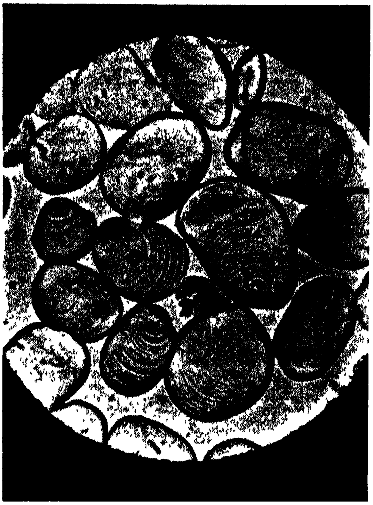

FIG. 1.
Tous-les-Mois or Canna Starch, from *Canna edulis*

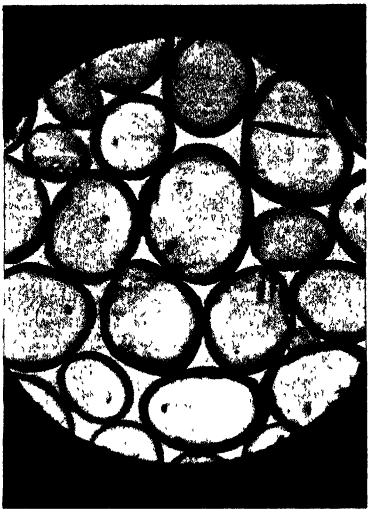

FIG. 2.
Potato Starch.

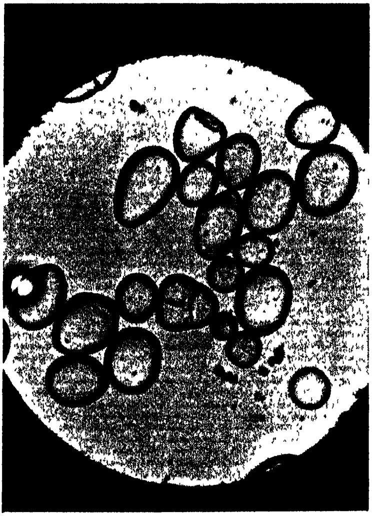

FIG. 3.
Potato Starch,

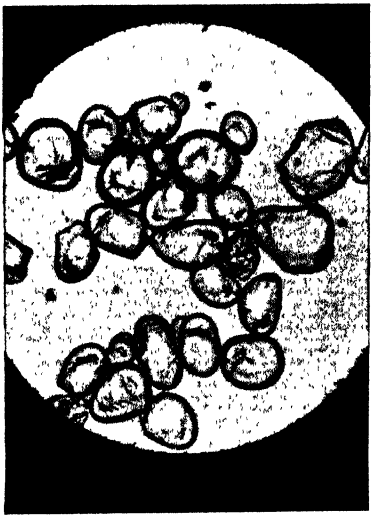

FIG. 4.
Sago Starch.

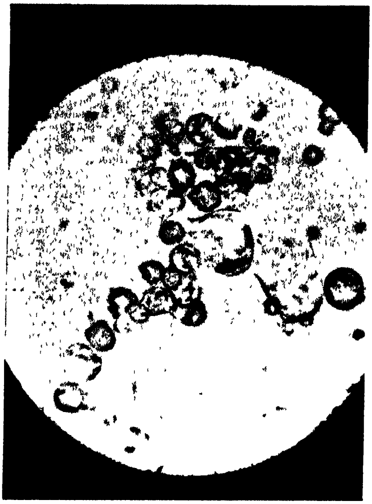

FIG. 5.
Prepared Sago.

Banana Starch, from *Musa paradisiaca*.

FIG. 7.
Curcuma Starch, or East Indian arrowroot.

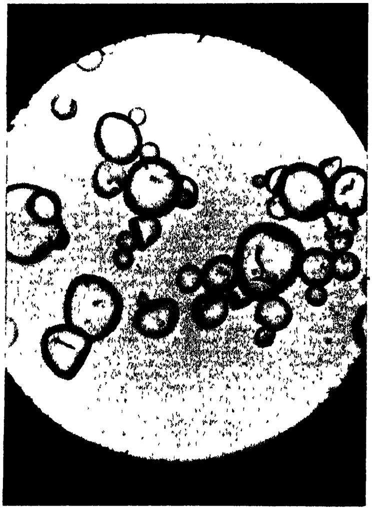

FIG. 8.
Florida arrowroot or Zamia Starch, from *Zamia floridana*.

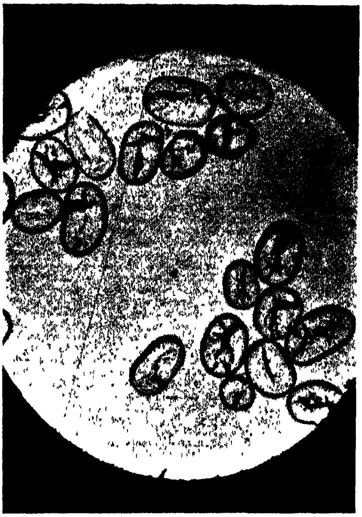

FIG. 9.
French Bean Starch from *Phaseolus vulgaris*

FIG. 10.
Maranta Starch or West Indian Arrowroot.

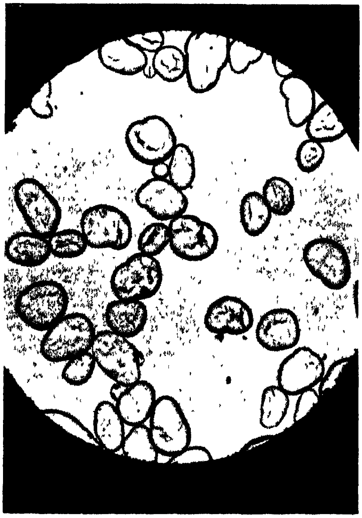

FIG. 11.
Pea Starch, from *Pisum sativum*.

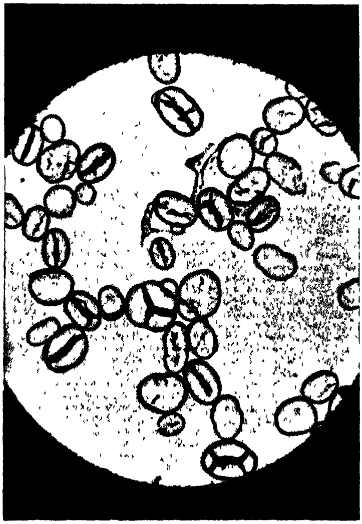

FIG. 12.
Lentil Starch, from *Lens esculenta*.

FIG. 13.
Broad Bean Starch from *Vicia faba*

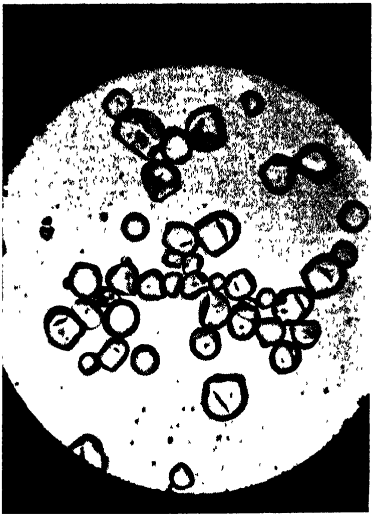

FIG. 14.
Tacca Starch or Tahiti arrowroot.

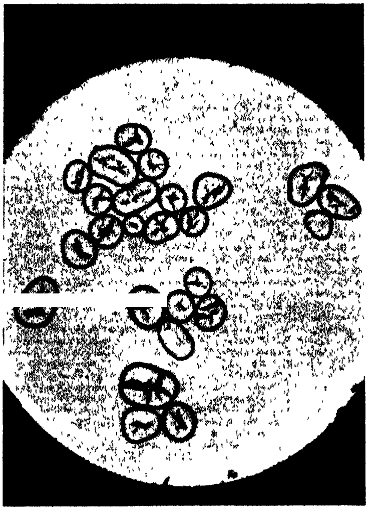

FIG. 15.
Scarlet Runner Bean Starch from *Phaseolus multiflorus.*

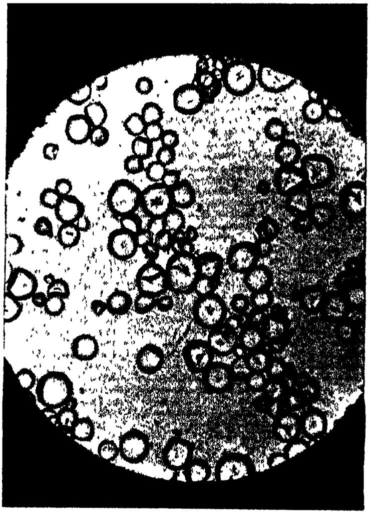

FIG. 16.
Manioc or Cassava or Tapioca Starch, from *Manihot utilissima.*

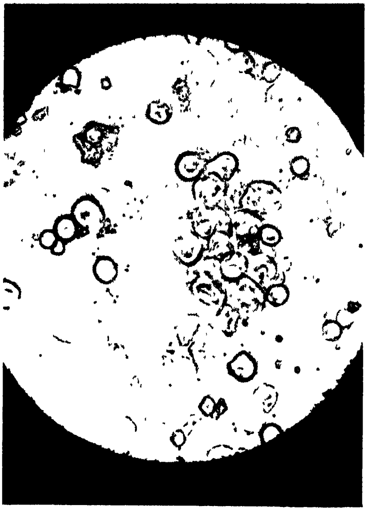

FIG. 17
Prepared Tapioca.

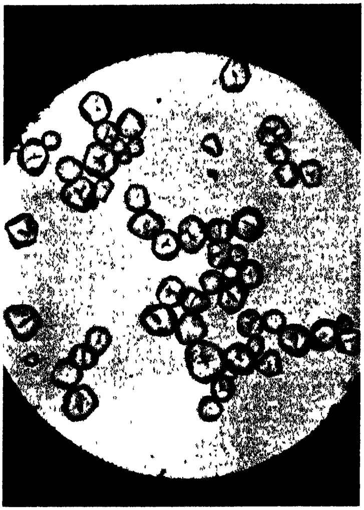

FIG. 18.
White Guinea Corn Millet Starch.

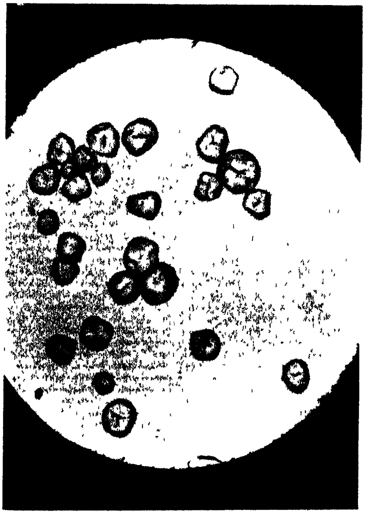

FIG. 19.
Dura Millet Starch

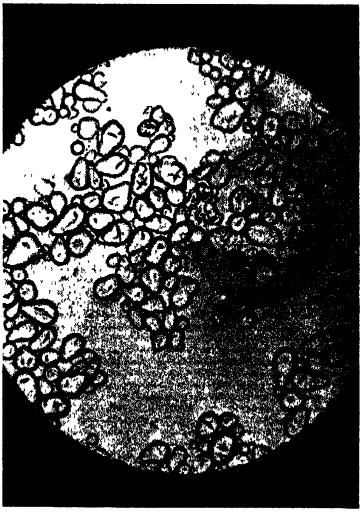

FIG. 20.
Horse Chestnut Starch from *Aesculus hippocastaneum.*

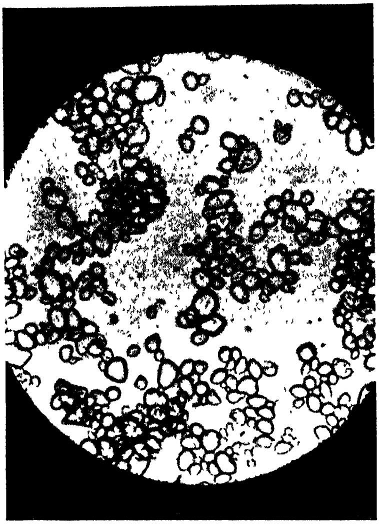

FIG. 21.
Acorn Starch

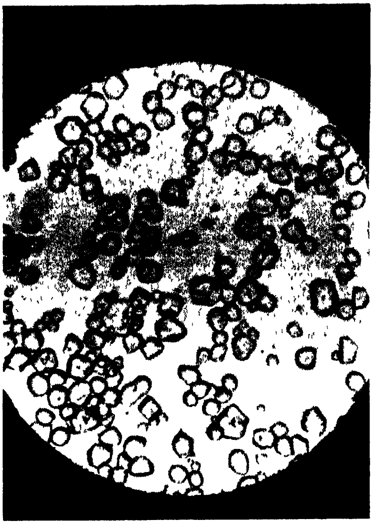

FIG. 22
Maize Starch.

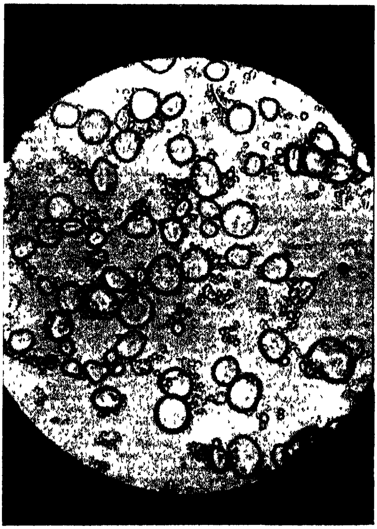

FIG. 23.
Barley Starch.

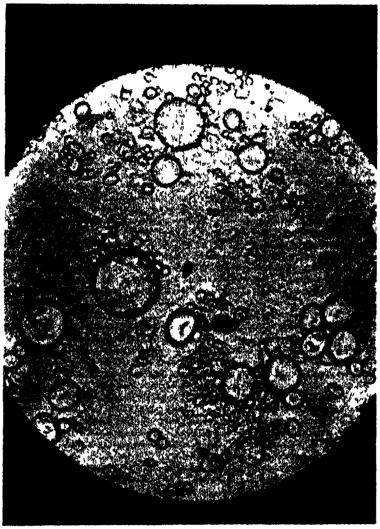

FIG. 24.
Rye Starch.

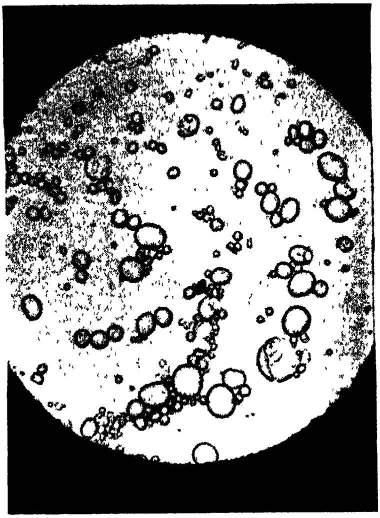

FIG. 25.
Wheat Starch.

FIG. 26.
Bulrush Millet Starch.

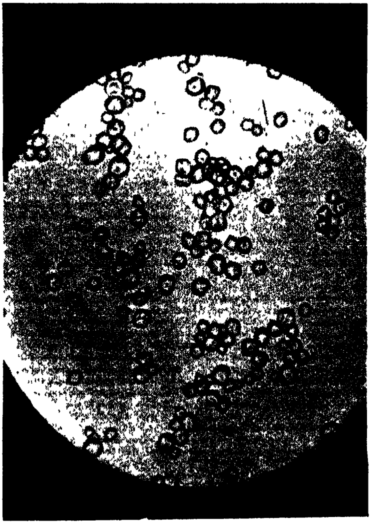

FIG. 27.
Shama Millet Starch.

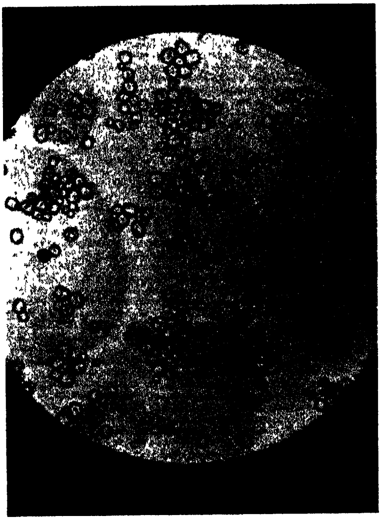

FIG. 28.
Italian Millet Starch

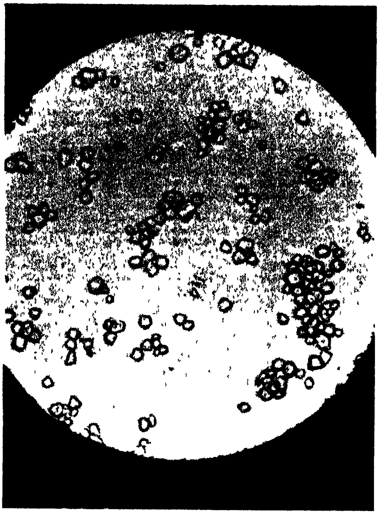

FIG. 29
Ragi Millet Starch

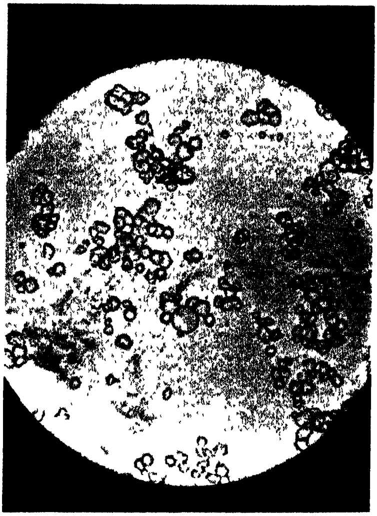

FIG. 30
Oat Starch

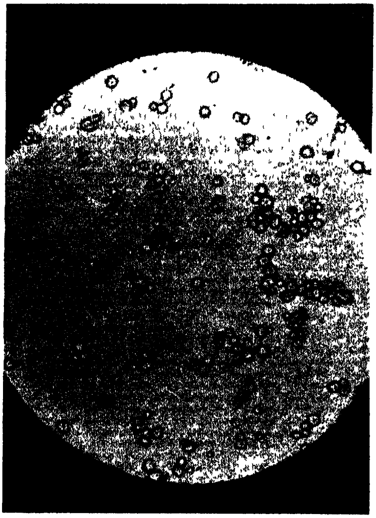

FIG. 31.
Buckwheat Starch.

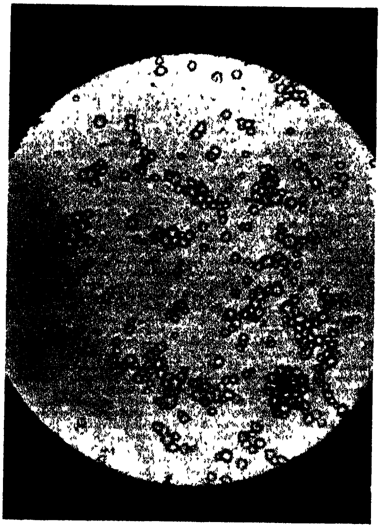

FIG. 32.
Rice Starch.

although the granule has a dense outer layer which on treatment with chromic acid exhibits radial fissures. The polarisation cross is seen only under high magnification.

*Colocasia esculenta.*—The granules of this starch are regular and oval and of size 10 to 55μ in length. The hilum is situated at the narrow end of the granule, the excentricity generally being about 1/6; it is distinctly seen in glycerol as a dark spot, less distinctly in water. It is characteristic of this starch that only the inner part of the granule appears to be striated, the striated part being surrounded by a thick homogeneous shell. On treatment with chromic acid the distinction between the shell and the striated interior is yet more marked. The polarisation cross is readily distinguished.

*Inocarpus edulis.*—The granules are mostly compound, consisting of two, three or more components which measure 6–27μ long by 4·5 to 22μ in breadth. Neither hilum nor striation is visible.

*Mangifera indica* (mango).—The granules are mostly compound, very few simple granules being observed. The former consist of two components of 5–25μ diameter. The hilum is especially distinct in glycerol; the striae are for the most part easily distinguishable.

*Nuellia pavale.*—This starch consists almost entirely of simple granules, very few compound granules being found. The latter consist of 2–4 components which resemble the simple granules in form, size and structure, and only occasionally show polyhedral flattening. The granules are 5–41μ in length, the breadth being ½–¾ of the length. The hilum cannot be seen in water, but is distinct in glycerol as a dark point; striae are not visible. On treatment with chromic acid a distinct radial fissuring occurs.

*Pachira aquatica.*—This starch is one of the few kinds that consist of semi-compound granules, i.e. granules consisting of components which are contained in a common envelope. The granules contain 2–6 components and measure from 4 to 16μ; their structure is best seen in glycerol; the hilum of each component then appears as a black spot.

*Phrynium dichotum.*—The granules are compound, consisting of 2–5 components which are partly spherical and partly polyhedral. The components are generally of unequal sizes ranging from 15 to 25$\mu$. The hilum is invisible or only faintly visible in water, but very distinctly seen in glycerol. The striae are only just perceptible in water and scarcely at all in glycerol.

*Sicyos angulata.*—The compound granules of this starch consist mostly of 2–8 components though the number may be as high as 28; the components are either polyhedral or partly polyhedral and partly spherical. The hilum and numerous striae are distinct.

According to P. E. Verkade,[1] the bulbs of various species of flowering plants have been utilised for the manufacture of starch.

## MICROSCOPICAL IDENTIFICATION OF STARCHES IN MIXTURES.

The microscopical detection of a particular kind of starch in a mixture of starches is quite impossible in many cases but methods have been devised in a few instances:—

*Detection of Maize Starch in Wheatmeal.*—According to a method proposed by K. Baumann[2] about 0·1 grm. of the meal is mixed with 10 c.c. of a 1·8 per cent. solution of potassium hydroxide, and the mixture is shaken at intervals during two minutes. The mixture is then treated with 4–5 drops of hydrochloric acid of 25 per cent. concentration and again shaken; it is necessary that the liquid should remain alkaline since the protein precipitate in acid solution would interfere with the subsequent microscopical examination. If a drop of the liquid is now placed on a slide and examined under the microscope it will be found that the wheat starch granules are completely ruptured whilst those of maize starch remain unaltered. A rough estimate of the proportions of the two starches may be made by comparing the treated mixture with similarly treated mixtures of the starches in known proportions.

The method is also applicable to the detection of maize starch in rye meal, the starch granules of the latter being

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[1] *Chem. Weekblad.*, 1918, **15**, 427.

[2] *Zeitsch. Nahr.-Genussm.*, 1899, **2**, 27.

ruptured by potassium hydroxide even more rapidly than wheat starch.

*Detection of Potato Starch in Wheat Meal.*—According to G. Blunck,[1] a portion of the sample is moistened with a drop of water on a microscope slide, dried and treated with a drop of a solution of the dye stuff "Metachrome red, G. Agfa." The excess of the dye stuff is washed off and the slide examined. Potato starch and cell tissues are coloured a bright golden yellow, whereas cereal starches are not coloured. The staining solution is prepared by cooling a solution of the dye in 30 per cent. alcohol, saturated at the boiling point, filtering and diluting the filtrate with one-fourth of its volume of water. In presence of acid the dye also colours wheat starch; hence in testing bread for the presence of potato starch, a small quantity of the crumb must first be treated with dilute alkali, and then washed thoroughly before adding the dye.

*Detection of Wheat Starch in Barley Starch.*—T. E. Wallis[2] states that the granules of barley starch never exceed 40$\mu$ in diameter whereas some wheat starches may attain a length of 45 or even 50$\mu$. Hence, the presence of granules over 40$\mu$ in length in a sample of barley starch indicates the presence of some other starch and would confirm the presence of wheat starch if this is suspected on other grounds.

*Detection of Wheat, Rye and Potato Starches in presence of each other.*—E. Unna[3] proposes the following method:—A mixture of 10 grms. of the flour with a 3 per cent. solution of phenol is allowed to stand for 24 hours. A portion of the mixture is then transferred to a microscope slide and left to dry at the ordinary temperature. The slide is then placed for 10 minutes in a mixture of Water Blue orcein-solution (orcein, 1; Water Blue, 1; glacial acetic acid, 5; glycerol 20; alcohol, 50, and water 23 per cent.), and eosin solution (eosin, 1; 60 per cent. alcohol, 99 per cent.). The slide is then washed, immersed for 15 minutes in 1 per cent. saffranin solution, well washed again and immersed for 30 minutes in a 0·5 per

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[1] *Zeitsch. Nahr.-Genussm.*, 1915, **29**, 246.

[2] *Pharm. J.*, 1922, **55**, 82.

[3] *Zeitsch. Nahr.-Genussm.*, 1918, **36**, 49.

cent. solution of potassium dichromate. The preparation is finally washed with water, then with alcohol, treated with xylene and mounted in Canada balsam. On microscopical examination it will be found that the potato starch is coloured dark red, the wheat starch pink, the rye starch yellow to brown and the gluten blue.

The following photomicrographs of the more important starches will prove a useful aid to identification; the magnification is 200 diameters in each case, and the starches are arranged as nearly as possible in decreasing order of size of granules.

# CHAPTER VI.

## MANUFACTURE OF POTATO STARCH.

THE centre of the potato-starch industry is a large area in Europe, comprising Germany, Holland, and Poland, and part of Russia, Czechoslovakia and France. The industry dates from about the middle of the eighteenth century, but not until the following century did it become firmly established. The rapid development of the textile and paper industries in the third decade of the nineteenth century opened new markets for starch, and a further impetus was given in the fifties by the application of starch sugar to the fermentation industries. At the present time the world's production of potato starch is probably between 300,000 and 400,000 tons. Most of this is absorbed by the producing countries, only Holland, Germany and Poland having any large export trade in potato starch. In 1924 Great Britain imported about 30,000 tons, of which more than half was obtained from Holland.

A feature of the potato starch industry is the large number of small agricultural factories which are engaged in it. In Germany for example, there are several hundred such factories, many of which produce only moist or "green" starch to serve as raw material for the manufacture of glucose or starch syrup. The small agricultural factories have been able to hold their own in spite of the competition of the large ones because they can obtain potatoes without much expense of transport and can easily dispose of their waste products, viz. exhausted pulp and effluent, the former as fodder, and the latter for the irrigation of land. To a large factory in a town, the costs of transport are heavy, and the waste products are an embarrassment

## THE RAW MATERIAL.

The composition of potatoes is subject to rather wide variations according to the conditions of climate and soil. According to Matzdorff, the percentage amounts of the different constituents in the whole tubers may vary between the following limits:—starch 10–30 per cent., sugars 0–5 per cent., pentosans up to 1 per cent., protein 0·6–3·5 per cent., total insoluble matters other than starch, 1·8–2·6 per cent., cellulose 0·8–1·4 per cent., ash 2–6 per cent., and acids up to 0·1 per cent. The kinds of potatoes best suited for the manufacture of starch are those possessing the following characters:—high starch-content, large size of starch granules, smooth thin skin, eyes not deeply sunken, low fibre-content and low content of soluble proteins. The starch-content of the potatoes used for starch manufacture usually ranges between 16 and 22 per cent., but in bad seasons it may fall to 14–15 per cent. or even lower. The size of the starch granules in potatoes influences the quality and yield of starch obtained, inasmuch as the best grades of commercial starch are those with the largest granules, and a high proportion of small granules (less than 0·02 mm. in diameter) in potatoes leads to an undue proportion of low-grade products and waste. The size of the granules is larger in some kinds of potatoes than in others, and larger in ripe than in unripe tubers. Smoothness of skin and regularity of shape facilitate the removal of dirt from the potatoes in the washing apparatus. A thin skin, and low fibre-content are desirable in order that the pulp may be uniform in texture and contain as little non-starchy solid matter as possible. According to Saare, a low protein-content in potatoes is an advantage in that it minimises the formation of froth during the factory operations. Potatoes which have been frozen, or are diseased, give rise to difficulties in the factory. They become soft and sometimes disintegrate in the wash; the starch deposits very slowly and imperfectly, and is liable to be discoloured.

The manufacture of potato starch is a seasonal industry. The working campaign commences with the harvesting of the potato crop, and often continues into the following spring, the factories operating on stored potatoes during the later portion of this period.

The conditions under which potatoes can be stored throughout the winter without excessive deterioration are well known, but not always easy to realise in practice. The worst dangers to be guarded against are on the one hand, frost, and on the other hand, undue warmth. Potatoes become frozen at -3° C., and as their dormant life is thereby destroyed, they rapidly become rotten after thawing. The best method of dealing with frozen potatoes is therefore to work them up in the factory as soon as possible. The dangers arising from undue warmth during storage are bacterial and fermentative developments, and a revival of the vital activities of the tubers, resulting in a rapid loss of starch and possibly sprouting. Even under the best conditions of storage, potatoes are subject to certain slow changes. The most important of these are evaporation of moisture, enzymatic formation of sugar at the expense of some of the starch, and a process of slow respiration by which sugar is destroyed. Temperature affects all these processes, but the second less than the others. In the neighbourhood of 0° C. evaporation and respiration are practically arrested, but the formation of sugar from starch still proceeds slowly, so that the potatoes become sweet. At 8–10° C. respiration keeps pace with sugar-formation, and at higher temperatures it proceeds more rapidly so that all sugar disappears. Rapid respiration produces a considerable amount of heat which, if not allowed to escape, will still further accelerate respiration and cause the potatoes to sprout. The best temperature for storage is 6–10° C.

The commonest method of storing potatoes for starch manufacture, is in long heaps of triangular cross section, 1–2 yards wide and 1½ yards high, known as clamps. The floor of the clamps is either level with the surrounding ground or sunk about a foot below it. The heaps are at first covered with a sloping layer of straw, which is prevented from blowing away by a few inches of soil. Under these conditions of comparatively free access of air, the potatoes are enabled to cool and the moisture which evaporates from them in considerable amounts during the first weeks is able to escape. After a month or two, when the risk of frost becomes serious, the heaps are covered in more thoroughly by additional layers of straw and earth, and in this condition they may remain until the following spring, when the warmer weather renders this mode of storage no longer safe. Large bulk silos are not suitable for storing potatoes for long periods, as it is difficult to ensure sufficient ventilation of the interior of the bulk to remove evaporated moisture and check any tendency to undue heating or sweating.

*Starch Value of Potatoes.*—Since the percentage of starch in potatoes is the chief factor in their value for starch manufacture, a rapid method for estimating this percentage is essential for purposes of valuation and proper factory control. The method used is based on the fact that the specific gravity of potatoes varies in close relationship with their contents of starch and of total solids, so that the latter values can be deduced approximately from the specific gravity. The determination of specific gravity is usually made by means of an apparatus known as a potato-balance which enables a weighed sample of the cleaned and dried potatoes (usually 5 kilograms) to be weighed again in a counterpoised metal basket suspended in a bucket of water. The apparent weight of the potatoes in water, subtracted from their weight in air, gives the weight of water which would occupy the same volume as the potatoes, and this divided into the weight of the potatoes in air yields the specific gravity. To save calculation, tables have been compiled from which the specific gravity, the percentage of total solids, and the starch value, can be ascertained immediately from the apparent weight of 5 kilograms of the sample in water. Table V represents in an abbreviated form, one compiled by Parow.

In a different type of apparatus for determining the specific gravity of potatoes, the volume of a given weight of the potatoes, e.g. 2 kilograms, is found by measuring the volume of water displaced when the potatoes are introduced into a container filled with water up to a certain level. With this apparatus also, calculations can be avoided by the use of tables showing the specific gravities and starch values corresponding to different volumes of water displaced.

The starch values found by the methods and tables described above are slightly in excess of the actual percentages of starch in the potatoes, as they comprise sugars as well as starch. According to Saare, 1·5 per cent. should be subtracted from the starch values to arrive at the actual percentage of starch, but a deduction of 1 per cent. is now believed to be more correct. For purposes of factory control and for the valuation of potatoes for starch manufacture it is usual to employ the starch values as given in the tables without any correction for sugar.

TABLE V.

INDICATIONS OF THE POTATO BALANCE AND CORRESPONDING COMPOSITION OF POTATOES (PAROW).

| Apparent weight of 5 kilograms of potatoes in water. grams. | Specific gravity. | Dry substance. per cent. | Starch value. per cent. |
|---|---|---|---|
| 290 | 1062 | 15·8 | 10·0 |
| 340 | 1073 | 18·3 | 12·5 |
| 390 | 1085 | 20·8 | 15·0 |
| 440 | 1097 | 23·3 | 17·5 |
| 490 | 1109 | 25·8 | 20·0 |
| 535 | 1120 | 28·3 | 22·5 |
| 580 | 1131 | 30·8 | 25·0 |
| 625 | 1143 | 33·3 | 27·5 |
| 670 | 1155 | 35·8 | 30·0 |

Potatoes used for the determination of specific gravity should first be carefully washed and wiped dry. The sample weighed out must of course be representative of the bulk, especially as regards the relative numbers of potatoes of different sizes. For the potato balance distilled water or condensed water from a steam engine should if possible be used, and it should be as near as possible to the standard temperature, 17·5° C. Maercker, who compiled a table of starch values on which those now in use are based, has stated that the starch values determined by means of the potato balance are usually accurate to within 1 per cent., but occasionally, errors of 2 per cent. or even more may occur when the composition of the potatoes is abnormal.

## OUTLINE OF MANUFACTURE.

The first stage in the manufacture of potato starch is the cleaning of the potatoes to remove adhering soil and dirt. This is effected in special washing apparatus, and is one of the most important operations in the factory. The next step is the complete disintegration of the cellular structure of the interior of the tubers in order to set free the starch granules which are enclosed in the minute cells. There is no purely chemical process known suitable for technical use by which the cell walls can be dissolved, and the starch set free. Biochemical methods have been proposed and used, but they have been abandoned. They involvc prolonged fermentative processes in which the potatoes are exposed to bacterial action, but they have been found difficult to control, and very offensive in operation and in the nature of their waste products. The method now in general use for setting free the starch is a purely mechanical one in which the potatoes are subjected to an intensive rasping process which reduces them to pulp and tears open most of the cells. This is effected by pressing the potatoes against the cylindrical surface of a rapidly revolving drum set with fine teeth. In many factories this operation is supplemented by a second similar one or by grinding the pulp between millstones.

The next step is the separation of the liberated starch from the pulped potatoes. This is invariably carried out by washing the pulp on sieves, usually with mechanical aids such as rapid shaking or the play of brushes on the sieves. The starch is thus washed through the sieves whilst the fibrous matters of the pulp remain behind. Where two raspers, or a rasper and a mill, are used in succession for pulping the potatoes, it is advisable to separate the greater part of the liberated starch after the first rasping, by washing on a fine sieve. This lightens the work of the mill or second rasper, and also that of the final washing-out sieves, enabling the latter to effect a very thorough exhaustion of the pulp.

The milky liquid, or raw starch milk, which passes through the sieves contains all the extracted starch, together with a small amount of fine fibrous matter and the whole of the soluble substances of the potato juice. There are three methods in use for separating the starch from this liquid. In the first, the starch milk is pumped into small settling vats and left undisturbed for 10–12 hours, during which the starch deposits as a compact layer. The supernatant liquor is then run off into large reservoirs in which the small quantity of very fine starch and impurities, still suspended in it, slowly deposit. The surface layer of the starch deposited in the settling vats is usually darker coloured than the underlying portions and contains a large proportion of fibrous and albuminoid impurities. This dark layer is in many cases removed by stirring it up with water without disturbing the underlying mass, and drawing off the resulting suspension, from which an inferior grade of starch is subsequently recovered. Instead of depositing the raw starch in settling vats, an alternative process is to allow the starch milk to flow slowly over very long, slightly inclined "tables" or "runs," about 3–4 feet wide, with raised edges. The starch is deposited more or less fractionally, i.e. the largest granules separate first, whilst smaller ones are carried farther before they are deposited, and the still lighter fibrous and albuminoid matters are mainly deposited at the lower end of the tables or carried away by the liquid. This method of sedimentation is very extensively used in starch manufacture. A third method of separating the starch from the raw starch milk is by the use of centrifugal separators.

The raw starch obtained by these methods is a compact mass, usually yellowish or greyish in colour. It contains a small quantity (less than 1 per cent. in most cases) of fibrous and other impurities. It is purified by being stirred thoroughly with water and allowed to deposit either in vats or on tables; these operations may be repeated several times according to circumstances, and the starch suspension may be passed through a fine silk sieve before deposition.

Many of the smaller factories in Germany do not carry the manufacture of potato starch beyond this point. The product, known as wet starch or green starch, contains about 50 per cent. of moisture, but it is compact enough to be filled into bags. For certain purposes, such as the manufacture of glucose or starch syrup, green starch is as suitable as the dry product, and not having to bear the cost of drying it is of course cheaper.

When dry starch is to be produced, the moist starch is first drained as completely as possible. This was formerly effected by placing the wet starch on tiles, but by means of centrifugal machines it is now possible to obtain starch cakes containing as little as 35 per cent. of moisture, and in this condition they can be broken up and introduced into the dryers. There are three main methods of drying employed for potato starch:—(1) drying on trays stacked in a chamber through which hot air is passed, (2) drying on a succession of moving bands in a large heated chamber, and (3) drying in revolving drums, with or without vacuum. The first method is the only one suitable for the production of lump starch, the last one reduces the starch to powder, and the second one also yields a small starch. Drying is carried out at a comparatively low temperature to avoid any gelatinisation of the starch. The final product contains as a rule 18–20 per cent. of moisture.

If the dried starch is to be sold in the form of powder, it is passed through a starch mill specially designed to pulverise without risk of gelatinising the granules by frictional heat. Finally the powdered starch is passed through a very fine silk sieve or bolting sieve.

In the following sections a more detailed account of the stages of manufacture will be given.

## Washing the Potatoes.

This is one of the most important operations in the factory, and unless it is carried out effectively the production of a perfectly white starch is impossible. When the potatoes arrive at the factory they carry an amount of adhering dirt which varies according to the character of the soil in which they have been grown. A stiff clay soil gives most trouble in the factory and necessitates a more or less prolonged soaking of the potatoes in water before the actual washing. In this case it is an advantage to be able to use water for the conveyance of the potatoes from the store to the washers, as this removes most of the adhering dirt and softens the remainder. When the soil is loose and crumbly, much of it can be removed before washing, by tumbling the potatoes over a sloping iron grating consisting of parallel iron bars about half-an-inch apart, or by passing them through an open-ended cylinder constructed of iron bars similarly spaced. Such apparatus is often installed at the point where the potatoes enter the factory.

Before the potatoes arrive at the main washing apparatus they are in some factories subjected to a preliminary washing. As already mentioned, this may be effected by conveying the potatoes from the store to the washer in a stream of water flowing along slightly sloping channels or flumes. In other cases the potatoes are transported by a spiral conveyor against a counter-current of water, and in others they pass through some simple form of preliminary washer. The main washer itself usually consists of a long, trough-shaped receptacle divided by transverse partitions into compartments in which the potatoes are kept in continuous movement, rubbing against one another, and slowly transported forwards through the successive compartments in turn, by means of rotating blades fixed to a horizontal shaft which extends through the whole apparatus. The trough is constructed of brickwork faced with cement, and is about 3 feet wide and 9–16 feet long, and divided into 3–5 compartments. The first compartment is known as the stone-catcher as most of the coarse soil and stones adhering to the potatoes are detached in it. Each compartment is provided with a false bottom consisting of a grating of iron bars about a quarter-of-an-inch apart, a few inches below the reach of the revolving blades. This grating may be flat or trough-shaped. The spaces below the gratings are provided with tightly fitting doors at the bottom for the removal of accumulated mud from time to time, and in some constructions these spaces taper downwards to a valved outlet through which the mud can be discharged while the apparatus is in operation. The transfer of potatoes from one compartment to the next is effected by means of scooped blades which, revolving on the central shaft close against the end wall of each compartment, lift some of the potatoes to the top of the wall so that they fall into the next compartment. The central shaft makes about 20 revs. per minute. Where water is plentiful, each compartment can be supplied independently, but in many cases fresh water is supplied only to the last compartment, from which it flows through the others in turn. As a rule, the potatoes are rinsed by jets of clean water as they are discharged from the apparatus, and in some types of washer they are similarly rinsed as they pass from each compartment to the next. A washing apparatus of the type described above, 16 feet long, has a capacity of about 25–30 tons of potatoes a day. Other types in use are in nearly all cases modifications of it. Illustrations of typical washers are shown in Figs. 33 (by Uhland) and 34 (by Jahn & Co.). Washers in which the potatoes are subjected to the action of brushes have a smaller output, and are not much used in starch factories. The amount of water consumed in the washing plant is usually between 400 and 1200 gallons per ton of potatoes.

## PULPING THE POTATOES.

In the rasping machines employed in starch manufacture the potatoes are reduced to pulp by rubbing against the toothed surface of a rapidly revolving drum mounted with its axis horizontal. In one form of apparatus, invented by Champonnois, the inner cylindrical surface of the drum is toothed, and the potatoes are introduced into the middle of the drum and thrown against the toothed surface by means of rotating beaters. This type of rasper has been much used in starch factories. In all other types, however, the drum is closed and the outer cylindrical surface is toothed. A hopper forming part of the casing of the apparatus, feeds the potatoes, together with about twice their weight of water, to the upper descending quadrant of the revolving surface of the drum,

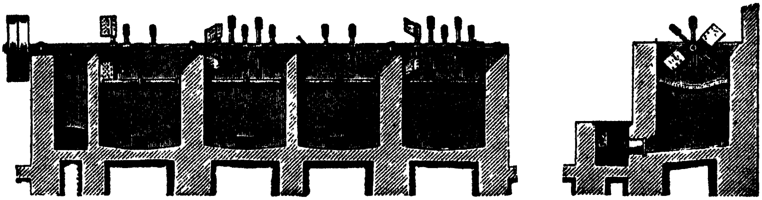


FIG. 33.

Sectional side and end views of a four-chambered potato-washer by Uhland.

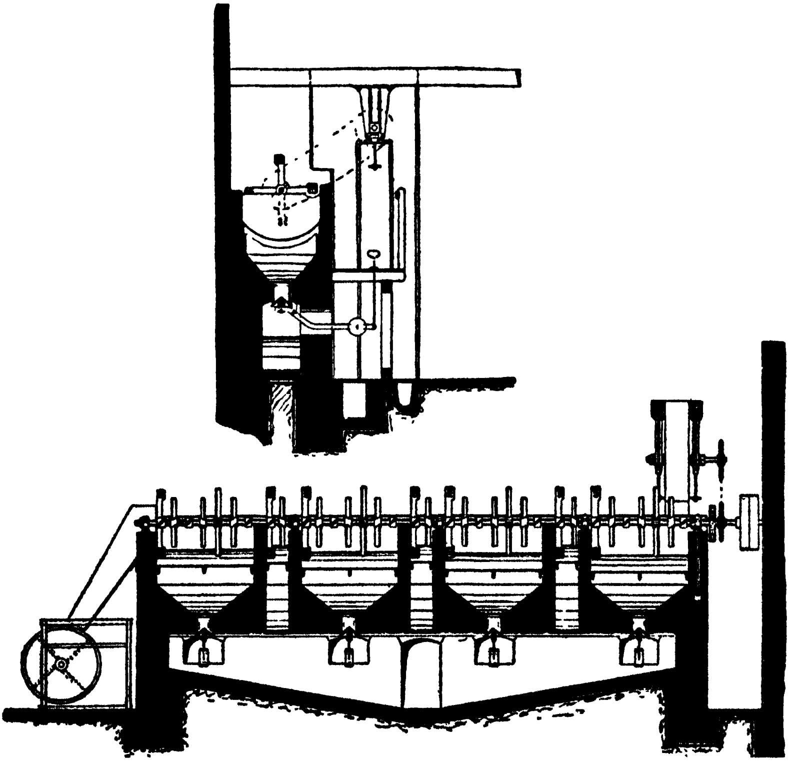


FIG. 34.

Sectional side and end views of a four-chambered potato-washer with intermediate draining chambers, by Jahn & Co.

and under pressure of their own weight they are reduced to pulp which is carried downwards by the revolving surface and made to pass between this surface and a block of hard wood set close against it, just below the hopper. The passage of the pulp between the drum and the block of wood effects a very thorough disintegration of the particles, and liberates the greater part of the starch from the cells of the potato tissue.

The rubbing surface of the drum may be provided with teeth in two different ways. In the older way the teeth are formed, like those of a rasp, by turning up the face of the metal with a punch. This type of rasper, although still to be found in some small starch factories, has several disadvantages compared with the "saw-blade" type described below. It is difficult to obtain uniformity in the size and arrangement of the teeth, and under the best conditions the pulp produced is not so fine nor so uniform as that produced by the saw-blade type of rasper. In the latter, which has for many years been the prevailing type, the cylindrical surface of the drum consists of a number of strips of wood or metal about half-an-inch wide, fixed firmly at the two ends of the drum, and holding tightly between them steel blades extending right across the drum with teeth like those of a saw along their edges. There are about eighteen teeth to the inch, and their points project only about one-twentieth of an inch beyond the surface of the drum. The fixing of the saw blades requires great care and experience. If the teeth of one blade project more than those of the others, the disintegrating action of the wooden block which presses against the drum will be seriously impaired. This block, which is made of a hard, short-grained wood, must be held in position very firmly. It is usually held by a strong iron clamp formed in one piece with the base-plate of the machine, and hand-screws are provided for adjusting its position relatively to the drum so that the right amount of pressure against the rubbing surface can be obtained. The saw blades are reversed after they have been in use a few days as the teeth get bent over with use. Very often the blades are serrated along both edges, and then they are used in four different positions. If stones find their way into the rasping machine with the potatoes they may work such havoc with the teeth as to necessitate dismantling the drum and replacing the blades. It is therefore customary to have a spare drum always ready for use. The size of the drums varies considerably according to the output required. For a factory working 5–6 tons of potatoes a day, a small drum of about 16–18 inches diameter suffices, but in large factories drums of twice this size are in use. The width is considerably less than the diameter, and usually does not exceed 12 inches. The drums revolve at a high speed, making about 1000 revolutions a minute, but in some machines this rate is considerably exceeded.

Various modifications have been made by different manufacturers, in the simple type of rasping machine as described above, with the object of increased efficiency. In some cases, for example, there are two wooden blocks, one below the other, instead of a single one. The space between the two blocks may be enclosed on all sides except that facing the drum; in this case it becomes filled with pulp which, having no other outlet, presses against the face of the revolving drum and acts as an elastic pad assisting materially in the disintegration of the pulp which passes between it and the drum face. In another type of rasper, the wooden block is replaced by a steel one with projections on its face. Some makers fit an auxiliary rubbing surface provided with saw blades, which has a concave curvature corresponding with that of the drum, and extends from below the wooden block round the lower part of the drum, close against the latter. In other types of rasper a somewhat similar auxiliary rubbing surface is perforated to allow fine pulp to pass through it, whilst retaining coarse particles until they have been sufficiently disintegrated. Figs. 35 and 36 show the general appearance and internal construction of saw blade raspers by Jahn & Co. These will work without water; those of medium size, with a drum 12 inches in width and 22 inches in diameter, have a capacity of about 4 tons of potatoes per hour.

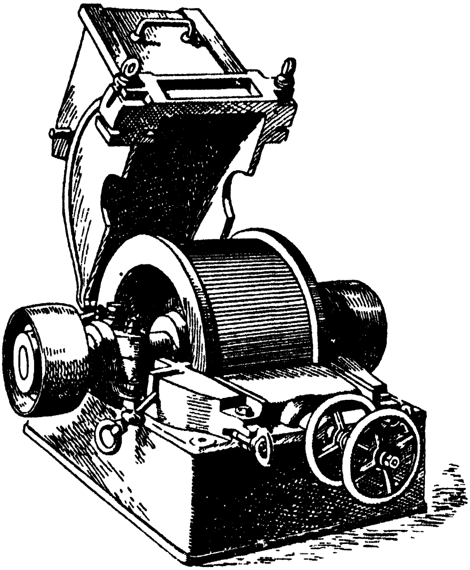


FIG. 35.

General view of a saw-blade rasper by Jahn & Co. The hinged upper portion of the casing, including the feeding hopper, is shown raised.

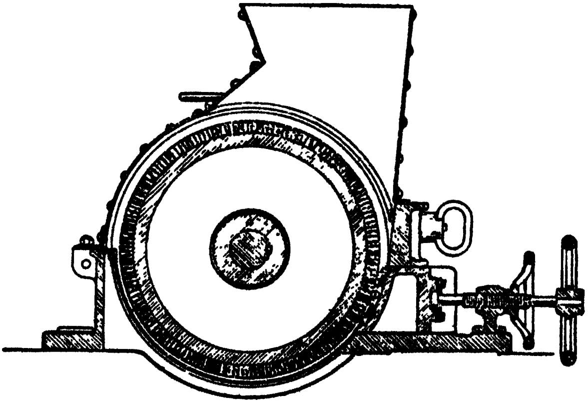


FIG. 36.

Sectional view of a saw-blade rasper by Jahn & Co.

Although a rasping machine may under the best conditions produce a pulp which requires no further disintegration, its maximum efficiency will not always be maintained in practice. Owing to the wearing of the teeth, or to unequal setting of the saw blades in the drum, or to accidental damage to some of the teeth, the pulp produced may contain too large a proportion of bound starch, i.e. starch enclosed in cells, to be neglected. Not infrequently the bound starch in pulp from the first rasper amounts to 2–3 per cent. of the weight of the potatoes worked. In many such cases it pays to subject the pulp to a second treatment, and in most factories such further treatment is applied as a general practice. Before the second disintegration, however, the pulp is usually washed on sieves to remove the greater part of the free starch. Various kinds of apparatus are used for the second disintegration. Grinding mills used to be the standard type in Germany, and they are still employed in many starch factories. These mills, having to deal with a wet material, differ in some respects from mills for the grinding of dry grain. There are two cylindrical millstones arranged horizontally. The lower stone is stationary, whilst the upper one rotates on a vertical shaft which passes through the centre of the lower stone and is keyed into the centre of the upper one. The upper surface of the lower stone is flat, but the lower surface of the upper one is scored with radial or sickle-shaped recesses extending from a central cavity to about two-thirds of the distance from the centre to the circumference of the stone, whilst the peripheral portion of the surface is flat. The central cavity in the upper stone is more or less conical in shape and extends to the top of the stone, where potato pulp to be ground is fed into it from a hopper. The diameter of the stones for mills of this type varies from about 2 feet to about 5 feet and the speed of rotation of the upper stone is on the average about 150 revolutions a minute. Such mills require about 1·5–3 H.P. to maintain them in operation, and about twice as much power to start them. In starting, the upper stone is raised out of contact with the lower one before it is rotated, and when it has attained full speed it is again lowered, and the pulp is fed into its central cavity. From this cavity it spreads out between the stones and ultimately escapes at the edges. These mills need careful supervision to give satisfactory results. Their efficiency depends on the amount of water in the pulp fed to them, on the degree of closeness of the two stones and the condition of their faces, and on the speed of revolution.

In many factories other forms of apparatus are used instead of mills, for the second disintegration of the pulp. In some cases a small rasper of the ordinary type, but with finer and more closely set teeth, is employed. Other types of saw-blade raspers, in which the rubbing surface is inside instead of outside the drum, have also been used. Among these is the well-known Champonnois rasper which has been used in French potato starch factories for the rasping of the whole potatoes. In this machine, the drum remains stationary, but there are inside it two blades which, revolving about 1000 times a minute, impose the same rate of revolution on the material charged into the drum, whether pulp or potatoes, and at this speed, centrifugal force causes the material to press against the toothed interior wall of the drum. Narrow slots between the saw blades allow the pulp, when sufficiently disintegrated, to escape into an outer casing.

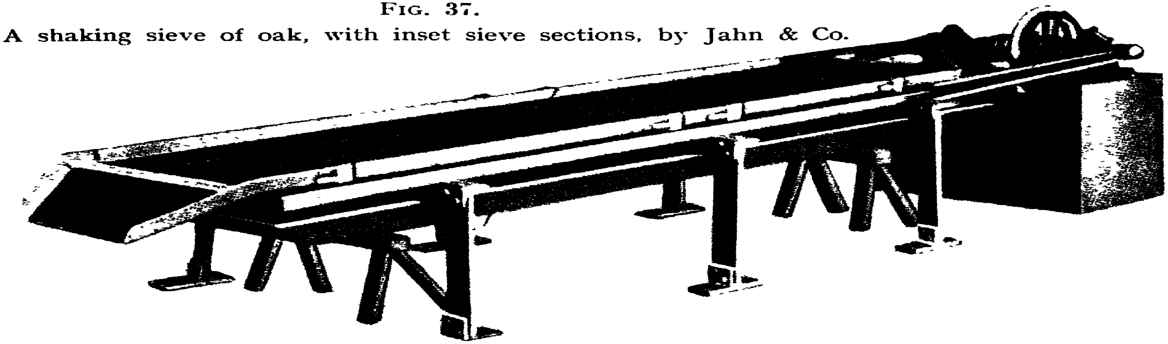
### SEPARATING THE STARCH FROM THE PULPED POTATOES.

The separation of the free starch from the potato pulp is invariably effected by washing the pulp on sieves. Two operations are usually involved. The first is the actual washing out of the starch from the pulp, for which relatively coarse sieves are used with holes about 1/75 or 1/50 inch in diameter. A considerable amount of fine fibre passes through these sieves, however, and in most factories the starch is afterwards passed through finer sieves to remove as much of this fibre as possible.

The main types of sieves employed in starch factories are as follows:—

(1) *Shaking Sieves.*—These are rectangular in shape, and are suspended or supported from below in such a manner

FIG. 37.
A shaking sieve of oak, with inset sieve sections, by Jahn & Co.



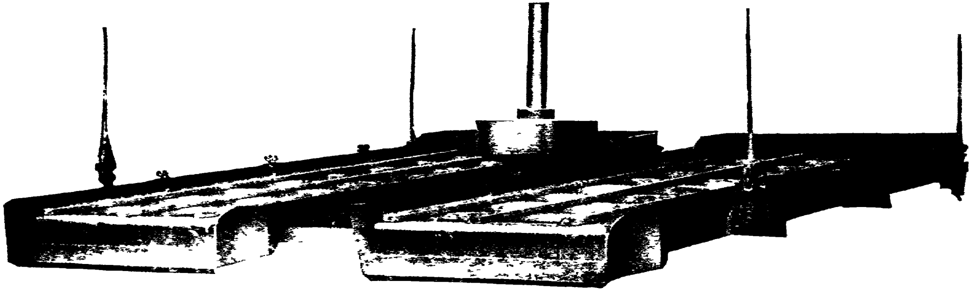


FIG. 38.
Twin shaking sieve by Uhland.

that a rapid oscillatory movement, usually up and down or backwards and forwards, can be communicated to them by some suitable device such as an excentric mechanism. They are mounted at an inclination of about 1 in 30 or 1 in 40. The material to be sifted is fed on to the upper end and, owing to the shaking of the sieve and the trickle of water from a system of perforated pipes usually overhead, the material travels towards the lower end, the starch meanwhile being washed through the sieve into a trough below. This type of sieve yields a starch much less contaminated with fibre than some of the other types described below, and it is therefore a useful refining sieve, but it is not so well adapted for the complete extraction of starch from a large mass of pulp. It is, however, often employed for the extraction of starch from the pulp between the first and second rasping or grinding, since complete extraction at this stage is not essential. When employed for this purpose, the sifting surface is formed of sheet copper with perforations about 1/50 inch in diameter, or of brass wire gauze of Nos. 35–45 mesh. The sieve oscillates several hundred times a minute and the displacement is not much more than an inch. The capacity of a shaking sieve 6–7 feet long and 2–2½ feet wide corresponds to about 25 cwt. of potatoes per hour. Sieves of this type consume more power than other kinds, and are noisy in operation. Their pores are also more liable to become clogged with fibre than those of other types which are provided with brushes.

Fig. 37 shows a shaking sieve of the usual form by Jahn & Co., constructed in lengths ranging from 8 to 16 feet, and 3 feet wide. The sieve surface is formed of a number of inset sections on pinewood frames, each of which is replaceable separately. Fig. 38 is a twin sieve by Uhland for washing out starch from pulp. The oscillatory motion is such that each point on the sieves describes a small circle. The pulp is sprinkled with water from transverse pipes at definite stages of its travel from end to end of the sieves.

(2) *Vat Sieves.*—These are large circular sieves, often 6–7 feet in diameter, consisting of brass wire gauze of No. 40 or

50 mesh stretched across the bottom of a circular wooden frame and supported below by a wooden grid to prevent bulging. A better form of construction substitutes for the single gauze surface a number of frame sections each covered with gauze, which fit closely side by side. With this arrangement, bulging of the gauze is obviated to a great extent, and a puncture or rent only involves the replacement of a single section. The pulp to be washed is fed on to the centre of the sieve. Suspended centrally from an overhead bearing is a vertical shaft carrying radial arms, to each of which a number of brushes are fixed at different distances from the centre. When the central shaft rotates, the brushes sweep over the surface of the sieve in circles, and being set at an angle they cause the pulp to travel slowly towards the circumference of the sieve where there are discharge outlets. Jets of water from overhead pipes play on the pulp meanwhile, and wash the starch through the sieve. Sieves of this type are widely used for the extraction of starch from pulp, but they are not good refining sieves as the brushes tend to push particles of fibre through the holes in the sieve. A vat sieve 7 feet in diameter has a capacity corresponding to about a ton of potatoes per hour.

(3) *Cylinder Sieves.*—These are of two kinds, viz. open or closed. The open ones are really half-cylinders, their sieve surface consisting of a long semi-cylindrical trough which is of course stationary. The closed cylinder sieves on the other hand are in most cases designed to revolve.

The open types of cylinder sieves have a rotatory shaft extending axially throughout their length and carrying radial arms with obliquely set brushes at their extremities. Pulp entering the sieve at one end travels forward at a rate which depends on the speed at which the shaft revolves and on the set of the brushes. Water is sprinkled on the pulp, particularly on the side of the sieve where the brushes ascend. The sieve surface is made of wire gauze, or preferably of perforated sheet copper, and beneath it is a receiving trough for the starch. A sieve of this type, 15 feet long, has a capacity corresponding to 1 ton of potatoes per hour. Such sieves are very efficient in extracting the starch from pulp, but they are unsuitable for refining purposes.

A more elaborate form of the open cylinder sieve is constructed by Jahn & Co. (see Fig 39). In this the sieve itself is stationary and there is a rotatory shaft, bearing radial arms, to the ends of which are fixed three or four long paddle boards extending the whole length of the sieve and edged with brushes which actually touch the sieve surface. There is also a spiral system of metal baffles fixed to the paddle boards, which cause the pulp to travel forward through the cylinder. Each paddle board as it rises lifts some of the pulp present in the sieve and brings it under lateral jets of water. After the paddle board has passed the top of its travel, the pulp falls back on the bottom of the sieve. This sieve is very efficient for the washing of pulp; a washing unit, consisting of two such sieves, one above another, has been designed, in which the pulp is passed first through the lower one and then through the upper. Fresh water is used in the upper one and the thin starch milk from this sieve serves as washing water for the sieve below it The capacity of the apparatus is about

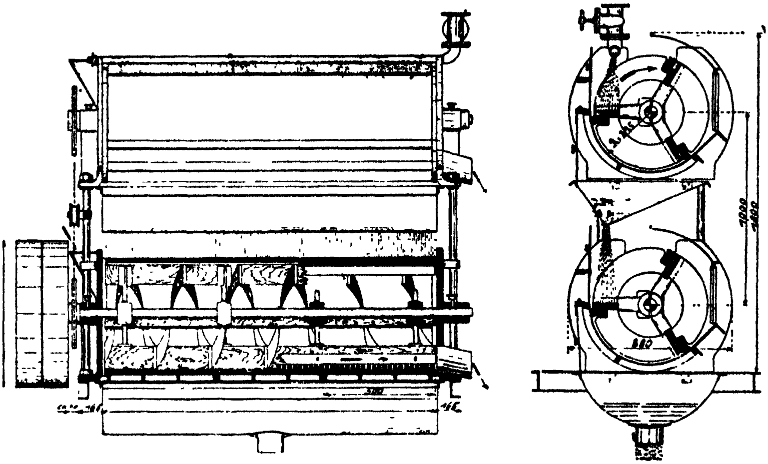


FIG. 39.

Pulp washing apparatus by Jahn & Co.

a ton of potatoes per hour, and the starch milk obtained has a specific gravity of 1·5–2° Baumé.

There are many different varieties of closed cylinder sieves. In these the cylinder itself revolves and the pulp, introduced at one end, is made to travel forward either by an inclination of the cylinder, or by suitable internal guide plates, or in another type by obliquely set brushes rotating in a direction opposite to that of the cylinder or in the same direction at a different rate. In all these sieves the pulp is watered by jets inside the cylinder, the central shaft itself acting as a water pipe in some cases. Sieves of this type, fitted with brushes, are suitable for washing out starch from pulp, and those without brushes make good refining sieves.

Considering the various types of sieves, it may be said that the types best suited for washing out the starch completely from potato pulp, are the vat sieves with brushes, the open cylinder sieves with brushes and the revolving closed cylinder sieves. The surface of the washing-out sieves may consist of sheet metal with holes 1/75–1/50 inch in diameter, or wire gauze Nos. 35–40 mesh, provided that the starch is afterwards passed through a fine sieve or refining sieve. If no refining sieve is used, the mesh of the washing-out sieve should be somewhat finer, corresponding to that of wire gauze No. 50. The most suitable types of refining sieves are the shaking sieves and the closed cylinder sieves without brushes. For these sieves wire gauze of Nos. 60–80 mesh, or silk gauze Nos. 5–8 should be used, and if a second refining sieve is employed it may have a mesh of 90–100 to the inch.

The pulping and sifting stations together require a large amount of water, about 2000 gallons per ton of potatoes pulped. The water should be clear, colourless and odourless, and free from iron salts.

## DEPOSITION OF THE RAW STARCH.

By the sifting operations described in the preceding section the starch is obtained in the form of a thin suspension known as the raw starch milk, which contains also a small amount of fine fibre and insoluble albuminoid matters, besides all the soluble constituents of the potato juice. These soluble substances from the juice tend to darken the colour of the starch if they remain long in contact with it, and it is therefore desirable to separate the starch from the accompanying liquid as soon as possible. This is usually effected by sedimentation in settling vats or on "tables" or "runs," but centrifugal separators are now employed in many factories.

*Sedimentation in Vats.*—This is the customary method in small factories, but it is not confined to these. The vats are about 4 feet high and constructed of masonry with a smooth facing of cement. The volume required per ton of potatoes worked is about 300 cubic feet. The raw starch milk is pumped into the vats and left to stand for 10–12 hours, after which the liquid is drawn off either by a siphon or by opening plugged outlets in the walls of the vats, or by means of a jointed or flexible tube connected with an outlet near the bottom of the vat and with its upper end supported at the surface of the liquid by a float, so that it descends as the level of the liquid descends, and always draws off the topmost layers.

*Sedimentation on Runs or Tables.*—The starch runs employed in this method of operation are tables usually about 60–100 feet in length, with a slight gradient so that starch milk will flow along them at a rate of about 4–8 inches per second. They are constructed of masonry faced with cement, or of wood. Their width varies from about 4 feet to 15 or 20 feet according to the daily output of starch. They are bordered by walls 1½–3 feet high. It is important that the starch milk should be fed uniformly over the whole width of the run at its upper end, and special distributing chests are employed for this purpose. As the starch milk flows down the run, a fractional sedimentation of the suspended matters takes place. At the upper end, heavy particles such as sand, and the largest starch granules are deposited. Farther along, purer starch is obtained, whilst at the lower end, very fine-grained starch is deposited together with a considerable amount of fibre. The liquid discharged at the end of the run contains a very small amount of fine-grained starch together with fibre and other impurities, and it is run into settling vats to allow this impure starch to deposit. This method of sedimentation has the advantage of a rapid separation of the starch from the accompanying liquid with its injurious constituents, and it also enables the starch from different parts of the table to be treated differently in the subsequent operations according to its degree of purity.

There are other processes for separating the raw starch from the starch milk, which are intermediate in character between the two described above. In some factories, settling vats of large area are used, in which there are partial dividing walls, operating as baffles, so that starch milk fed continuously into the vat at one point, has to pursue a long circuitous course before it arrives at the point of discharge, and in the course of its travel the starch is deposited.

Within recent years centrifugal machines have been used in some factories in place of settling vats and tables, for the separation of raw starch from the raw starch milk. Centrifuges provided with a perforated basket lined with filter cloth have long been used for the draining of purified starch and also to some extent as a means of purification; it is possible by means of them, to obtain the starch in a drier condition than by sedimentation under the influence of gravity. These centrifuges, however, are not so suitable for the treatment of raw starch milk, on account of frothing and other disadvantages. Centrifuges with imperforate drums are used for raw starch milk in some factories. In these the starch is deposited against the walls of the drum leaving the liquid as an inner stratum. The apparatus is provided with a pipe through which this separated liquid can be discharged whilst the drum is spinning; and further quantities of raw starch milk can be introduced until the layer of deposited starch more than half fills the drum, whereupon the latter is brought to rest and the starch is discharged for purification.

There are other types of centrifugal machines in which the deposited starch as well as the liquor can be discharged continuously whilst the apparatus is in rotation Jahn's centrifugal separator (see Figs. 40 and 41) is of this type. The

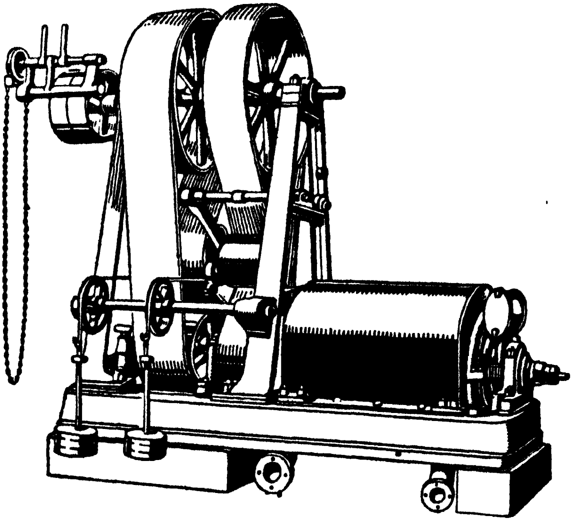


FIG. 40.

Jahn's centrifugal separator.

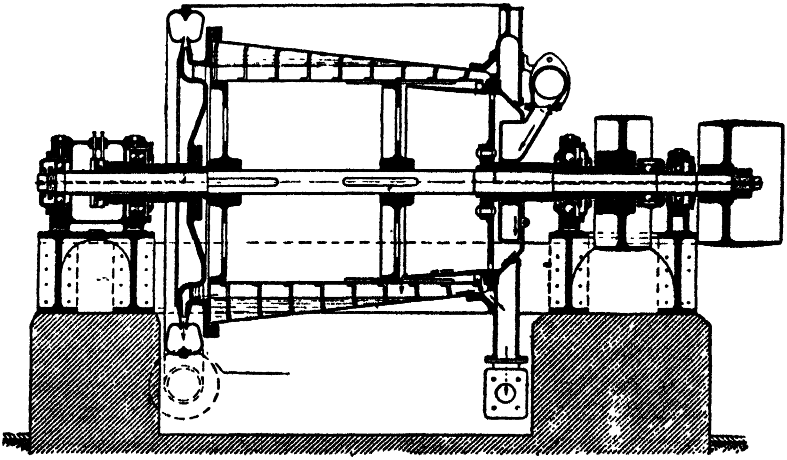


FIG. 41.

Sectional view of Jahn's centrifugal separator.

rotating chamber is somewhat conical in shape and mounted with its axis horizontal. The raw starch milk of specific gravity 3° Baumé, or less, enters the rotating chamber at its narrow end, whilst the separated liquor, containing the lighter impurities is discharged from the wide end. The starch is deposited against the walls of the chamber and is conveyed slowly but continuously to the narrow end by means of a worm conveying thread which rotates close against the walls of the chamber at a rate slightly different from that of the chamber itself. It is discharged at the narrow end with a moisture-content of about 55 per cent., and is immediately thinned with sufficient water to enable it to be pumped to the sieves or washing vessels. The apparatus has a capacity of 10 cubic metres per hour and consumes 8 horse power. It saves a great amount of time and renders unnecessary the raw starch settling vats and the labour associated with them.

### Purification of the Raw Starch.

The raw starch from the settling vats or tables is a compact mass, firm enough to be handled with a spade. If it has settled well it contains about 50–60 per cent. of moisture. It has a somewhat brownish yellow or grey tint and contains impurities which may amount to as little as 0·2 per cent.; but which often exceed 1 per cent. in factories where the raw starch milk has not been passed through fine sieves.

The raw starch is purified by washing with water, followed by sedimentation either in the washing vat itself or on tables. The washing vat is constructed of wood, iron or cement-faced masonry, and is usually cylindrical in shape. The diameter varies from 6 to 10 feet, and the height from 3 to 4 feet. In some cases the vat can be tilted, but if this is not the case, the floor slopes downwards towards a cleaning outlet. A vertical spindle extends downwards from an overhead bearing into the centre of the vat, and carries two stirring blades which are preferably adjustable in height, so that when necessary they can be raised during the settling of the starch, and lowered when it is necessary to stir up the deposited mass (see Figs. 42 and 43). In this vat the raw starch is stirred with about twice its bulk of water for an hour and then, if the whole purification process is to be carried out in the vat, the starch is left for 6–10 hours to settle. Heavy particles, such as sand, are deposited first, followed by the bulk of the starch. Particles of fibre and protein, being much lighter than the starch granules, remain longer in suspension, and, together with the smallest starch granules, they form a comparatively dark coloured and loose layer above the compact deposit of starch. After sedimentation is complete, the liquid is drawn off, usually through a vertically sliding door in the side of the vat. The dark coloured layer above the starch is then stirred up with a little water, without disturbing the underlying pure starch, and drawn off for separate purification. The starch remaining in the vat is again stirred up with water, and the whole series of operations is repeated once or twice.

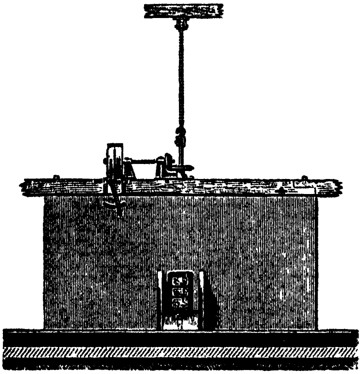


FIG. 42.

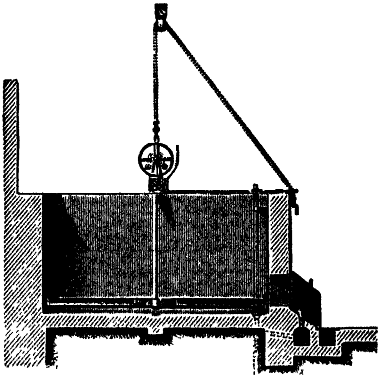


FIG. 43.

FIGS. 42 and 43. Front elevation and side section of starch washing vat by Uhland.

If the raw starch is to be purified on runs or tables, it is first stirred with water in a mixing vat, as already described, and in some cases it is passed through a fine sieve, especially if it has not been subjected to this treatment previously. The tables used for starch purification are usually of wood, about 50–80 feet long, 4–6 feet wide, and provided with walls about 18 inches high. The difference in level between the upper and lower ends is usually less than an inch, but the gradient can be adjusted by levelling-screws at intervals along its length. Before the starch milk is run on to the tables it is in many factories passed through a small mixing vessel to render it uniform in concentration. At the upper end of the table there is a distributing box to ensure that the starch milk is fed evenly over the whole width of the table, and an operator keeps watch on the table to smooth out any inequalities in the depth of the deposited layer. The rate of flow of the liquid along the table is about 6–8 inches per second. The deposit is allowed to accumulate until it is about a foot in thickness. The water which flows away contains some small starch, together with impurities, and is allowed to stand in vats for this impure starch to settle. The starch deposited on the tables is usually subjected to a second sedimentation, which is sometimes preceded by a screening operation with fine sieves of about 100 mesh.

It is now a common practice, especially in the production of dry starch, to supplement the methods of purification described above by a treatment in centrifugal machines. This not only yields a starch containing less water than that deposited in vats or on tables, but it also has a purifying action, and in some factories it has partially replaced the ordinary sedimentation processes. The centrifugal machines employed for this purpose have a drum or basket of perforated steel, about 1½–3 feet in diameter, lined inside with strong wire gauze, fine gauze, and finally, filter cloth. In some machines the peripheral portion of the basket is divided into compartments by removable radial partitions, to facilitate the removal of the starch cake. The speed of rotation of the basket is about 1000 revolutions a minute. The starch to be centrifuged is mixed with sufficient water to form a thick suspension of about 22° Baumé (sp. gr. 1180). For this purpose a stirring vat is usually installed above the centrifuges so that the thick starch milk can be run into the latter as required. The charge for a centrifuge varies from 2 to 5 cwts. according to the capacity of the drum or basket. During the rotation, the starch is deposited against the filter cloth lining the walls. The radial insets or partitions, referred to on p. 122, enable the starch cake to be easily removed in sectors. If there is a discoloured layer of impure starch on the inner surface of the cake, this is scraped off before the cake is removed. Usually four charges can be worked through in an hour, and assuming the cake to be 4 inches thick, this corresponds to an output of 250 kilograms (5 cwts.) of moist starch (containing 35–40 per cent. of moisture) per sq. metre of filtering surface per hour. A centrifuge constructed by W. H. Uhland is shown in Fig. 44.

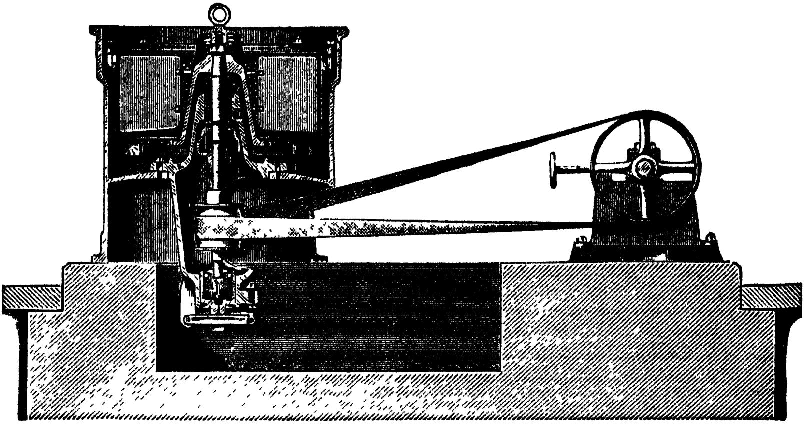


FIG. 44.
Starch centrifuge with perforated basket, by Uhland.

The total amount of water required for the purification of raw starch usually ranges from 200 to 600 gallons per ton of potatoes worked.

## SPECIAL DIFFICULTIES IN MANUFACTURE.

In the extraction and purification of potato starch, certain difficulties are liable to be encountered, which require special treatment. One of these is the formation of a persistent froth especially during the rasping and sifting operations.

According to Saare this is chiefly due to the presence of albuminoid matters, and although there appears to be no satisfactory method of avoiding it entirely, it may be minimised by a liberal supply of water during rasping and sifting, by a thorough washing-out of the raw starch from the pulp before the latter goes to the mills or the second rasper, and by avoiding unnecessary pumping or splashing of the raw starch milk.

Another frequent difficulty is due to abnormally slow and imperfect deposition of the starch. The rate of subsidence of starch and the compactness of the deposit formed are influenced by various factors and especially by the presence of certain impurities. Pure starch separates from pure water in a denser layer than from water containing potato juice; hence the more water there is in a raw starch milk the more compact will be the deposited starch. The presence of fine fibrous matter is also detrimental to sedimentation. Saare compared the deposit formed by pure starch with that formed by starch containing 1 per cent. of fibre, and found that in the former case the deposited starch contained 48·5 per cent. of water, and in the latter case, 55 per cent. This illustrates the importance of freeing the raw starch from fibre by fine sifting at as early a stage as possible. More serious difficulties in sedimentation are apt to arise in working diseased, putrid or frozen potatoes. In such cases the starch deposit may be half-fluid instead of firm and compact.

Unsatisfactory deposition of starch which is not cured by copious dilution of the starch milk or by removal of fibre may often be remedied by addition of certain chemical agents such as sulphuric or sulphurous acid, or if these fail caustic soda may be effective. Other chemicals which have been used either to assist sedimentation or to improve the appearance of the starch are sulphites, bleaching powder with or without acid, chlorine and sodium carbonate. For certain applications of starch, especially in textile work, the presence of even minute quantities of some of these chemicals might be harmful. It is accordingly one of the rules of the Hamburg starch market that potato starch cannot be graded as of first quality (*Prima* starch) unless it is free from chlorine and acid. Under normal conditions the use of sulphuric acid for such starch is now comparatively rare, as the acid is not easy to remove entirely by washing, but it is not infrequently employed in working up impure starch fractions obtained in ordinary factory practice. Bleaching powder and hypochlorites are not widely used.

The chemical agent most frequently employed in potato starch manufacture is sulphurous acid or its salts, such as calcium bisulphite. The treatment is usually applied to the raw starch when it is being mixed with water preparatory to the first sedimentation. According to Saare the rate of subsidence of raw starch and the compactness of the deposit are decidedly improved by addition of as little as 8–26 grms. per 100 kilos, i.e. 0·008–0·026 per cent. of sulphur dioxide. This is the case with starch from sound potatoes, but the colour of the starch is not improved, being very satisfactory without the treatment. In the case of starch from diseased or frozen potatoes the beneficial effects are naturally much more pronounced. Addition of sulphurous acid to the raw starch milk or to the pulp in the rasping apparatus not only improves the subsequent deposition of the starch, but also checks the customary darkening of the potato juice.

Chlorine and ozone have been used as bleaching agents for starch, and ultramarine or other blue colouring matter is sometimes added to produce a brilliant white appearance.

## WORKING UP LOW-GRADE FRACTIONS.

In the factory operations as already described, there is obtained at each stage of purification of starch a low-grade fraction containing the separated impurities. The more or less coloured starch scraped or washed off from the main starch deposits in the washing vats or centrifuges, and also that deposited from the liquors which flow from the refining tables when these liquors are allowed to stand at rest, contain about 3–5 per cent. of impurities, calculated on the dry solids. This impure starch is purified by means of sieves, preferably of the shaking type, but as it consists mainly of smaller granules than the main starch fractions, the sieves employed are of extra fine mesh. Silk gauze is preferable to wire gauze of the same mesh as it retains fibre better than the latter. After passing through the sieves the starch is deposited on tables. On account of the small size of the starch granules, the flow of the liquid must be slower than in the case of first-product starch; it is usually about 3–5 inches per second. The deposited starch from the tables may be added to the next lot of raw starch, and purified with this, or it may be purified by itself, in which case sulphurous acid or other chemical agent is usually employed.

A much more impure starch fraction is represented by the matter deposited in the large reservoirs, usually in the open air, into which all the impure liquors from the original raw starch milk and from the purification of low-grade starch are conducted. These liquors, which contain albuminoid substances, are liable to fermentation and putrefaction. The deposit which separates from them is worked up only at long intervals, and in some cases not until the end of the campaign. It is accordingly dark in colour and malodorous, and often semi-fluid in consistency. It is subjected to the same kind of purification processes as the fraction already described, but with certain differences. Owing to the extremely small size of the starch granules very fine sieves are employed, and on the settling tables a very thin suspension is usual, and the rate of flow is very slow. The use of chemicals is often necessary to obtain satisfactory sedimentation. Sulphuric acid is most commonly employed, but hydrochloric acid, bleaching powder, caustic soda and calcium bisulphite have also been used. The best of the starch obtained from this sludge is only of second quality, and sometimes a third quality is produced as well. The final residue, which cannot economically be worked up for starch, is sometimes drained centrifugally and used for the manufacture of glucose syrup.

The liquors drawn off from the large reservoirs in which the last-mentioned starch sludge has deposited, contain usually about 0·2–0·6 per cent. of solid matters in solution. Their disposal is often a matter of considerable difficulty for they are a breeding ground for yeasts and bacteria. They contain all the soluble matters from the potatoes, including nitrogenous substances, potash and phosphates, and in agricultural districts they are accordingly often disposed of in irrigating land.

### DRYING THE STARCH.

Starch which is to be dried is usually collected in centrifuges as the final step in the purification processes, by which means the moisture-content can be reduced to less than 40 per cent. In this condition the starch can be broken up into small fragments, which is desirable when powdered starch is to be produced. There are specially designed disintegrators for breaking up the centrifugal starch, but very often a coarse vat sieve with revolving brushes is employed. When lump starch is to be produced, the centrifuged starch can be sufficiently broken up by hand or by the conveyors from the centrifuge to the drying plant.

The drying of starch must be carried out at a comparatively low temperature, preferably below 40° C. Above this temperature, moist starch is liable to develop fissures in some of the larger granules, which impair the lustre of the dried product, and at still higher temperatures some of the granules become partially gelatinised, forming small lumps which cannot be powdered. According to Brown and Heron, the adhesive power of starch paste depends on the temperature at which the starch has been dried, high temperatures reducing the adhesive power.

There are several different systems employed for drying starch, the most important of which are described below.

*Drying on Trays.*—This method of drying is usually carried out in a large drying room about 10 feet high in which there are stacks of trays, with gangways between. The trays are supported at vertical distances of about 6 inches from one another, and are formed of canvas or stout paper stretched on frames about 4–5 feet long and 3 feet wide. Each holds a charge representing 4–8 lb. of dry starch. The air in the room is heated by hot water or steam pipes close to the floor and sometimes also at half the height of the room. Exhaust steam from the factory engine is usually employed for heating the pipes. The air inlets are at the bottom, and the outlets in the roof, and in some cases these are provided with fans to assist the natural draught. A factory working 50 tons of potatoes per day of 24 hours would require a drying room of about 3000 cubic yards capacity, containing nearly 4000 trays. The usual time required for drying is about 20–24 hours for the lower trays and twice as long for the upper ones. Drying plants of this kind are operated continuously, individual trays being withdrawn and recharged as soon as the starch on them is dry. There is a somewhat different type of plant, with much smaller drying chambers, in which the whole space, including the gangways, is utilised for the stacking of the trays. In these chambers there is much less difference between the rate of drying at the top and the bottom, and all the trays are stacked at the same time and withdrawn at the same time.

Drying on trays is particularly suited for the production of lump starch, but it requires a large amount of space and is very slow. It is less used than it was formerly, as the powdered form of potato starch is now more in demand than the lump form. Another method of drying on trays, which is much more rapid than those described above, is employed in some factories. This is the so-called tunnel drying. Stacks of trays mounted on trolleys are moved slowly through a tunnel about 30 feet long, through which a current of warm dry air passes in the opposite direction. The time required for the starch to pass through the tunnel is usually about 3–4 hours. A tunnel drier, constructed by W. H. Uhland is shown in Fig. 45.

*Drying on Moving Belts.*—This system is very extensively employed, as it is economical in respect of space and labour The moist starch, broken into fragments as uniform in size as possible, is fed through the top of a large drying chamber in which it falls on the uppermost of a number of moving cloth surfaces extending, one above another, almost from end to end of the chamber. Each cloth is an endless band 4–5 feet wide, passing tautly round two revolving rollers, one at each end. After being carried to the limit of travel of the top band, the starch falls on to the projecting end of the one next below which is travelling in the opposite direction. Arrived at the limit of travel of this band, the starch falls on to the projecting end of the next lower one, and so on, until having been carried backwards and forwards from end to end of the chamber, it is discharged dry from an outlet at the bottom. The length of the bands may be 20–30 feet and the number of bands 12–30. Between the upper and lower stretch of each band there are at intervals flat heating pockets, or coiled-pipes supplied with steam or hot water, so that the bands are heated. The temperature of the starch should, however, not rise much above 30° C., while it is still moist. According to Saare an apparatus of this kind with 15 bands 1·38 metres wide and of 10·5 metres working length, yields 10 tons of dry starch in a day of 20–22 hours, the starch taking 25–30 minutes to pass through the apparatus. This system of drying requires the moist starch to be broken up uniformly into small particles, and for this purpose a brush sieve is commonly used. A belt dryer, constructed by Jahn & Co. is shown in Fig. 46.

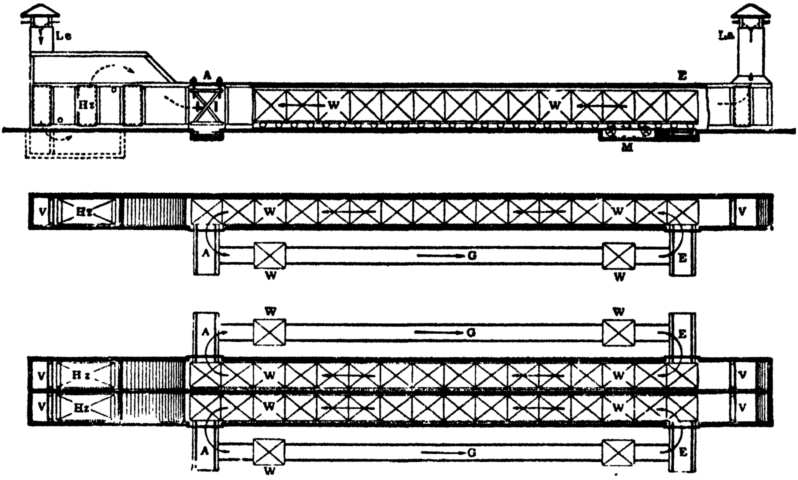


Fig. 45.

Sectional elevation and plans of tunnel drying plant by Uhland.

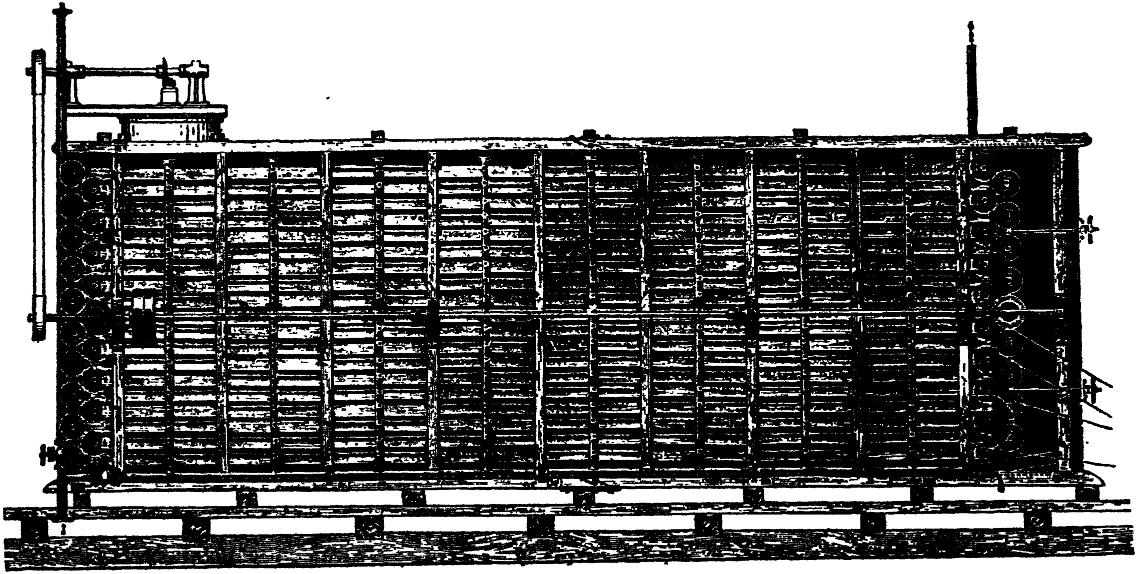


FIG. 46.

View of interior of moving-belt dryer by Jahn & Co.

*Drying in Drums.*—This system is suited only to the production of powdered starch, since the material is kept in constant motion during the drying process, and any lumps are thus broken up. A well known apparatus of this type is Fehrmann's dryer in which starch contained in a long closed casing is continuously stirred by a revolving system of five coaxial cylindrical frames consisting of spaced wooden laths. These frames revolve about five times in a minute. The casing, 12–24 feet long, 6 feet wide and 9–10 feet high, is slightly inclined so that the starch travels from end to end. The drying of the starch is effected by passing into the drum a current of air previously heated by a tubular heater.

*Vacuum Drying.*—This is a development of the system of drying in drums. It has the double advantage of hastening the evaporation of moisture and lowering the temperature at which evaporation takes place. Uhland's vacuum drying plant, shown in Fig. 47, consists of a steam-jacketed cylinder in which there are rotating bundles of steam tubes studded with lifting and transporting shovels by which the starch is kept in continuous motion. The escaping vapours pass first through a dust-collecting chamber in which most of the fine starch carried by them is deposited, and then the vapours are condensed in cooling tubes, and the starch still held by them can be recovered. The capacity of these dryers ranges from 5 cwts. upwards.

The type of dryer most suitable for any given factory, depends on a number of factors. If lump starch is required, some form of tray dryer must be used. If the final product is to be powdered starch, drum dryers have the advantage that they themselves effect a pulverisation of the starch. Tray dryers require much more space and manual labour than the other types, but on the other hand they consume less mechanical power. In all forms of dryers there is some risk of the formation of partly gelatinised lumps due to local overheating of the starch whilst still moist. This risk is least in the drum dryers, where the continuous stirring of the starch ensures fairly uniform drying, and in vacuum dryers, where the moisture evaporates at a much lower temperature than it would do under atmospheric pressure. In tray dryers the circulation of air is often very imperfect, and the trays nearest to the hot water pipes are liable to become unduly hot. Gelatinisation is most to be feared, however, in the moving belt dryers, where the heating elements immediately under the moving bands sometimes overheat the starch.

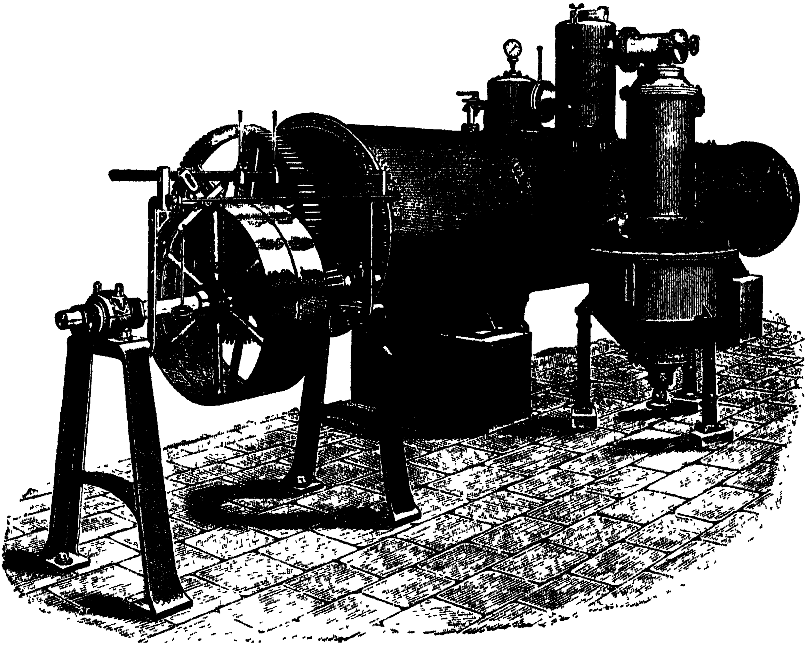


Fig. 47.

Vacuum dryer by Uhland.

## Powdering and Bolting the Dried Starch.

Potato starch is now more commonly marketed in powder than in any other form, and it is essential that the powder should be quite free from lumps. Starch which has been dried in drums, with or without vacuum, is already in the form of powder, but it needs sifting or bolting. Starch from other forms of dryers requires to be passed through a starch mill before bolting. It is often convenient, however, to pass it through a bolting machine first, as many of the lumps are thereby broken up and only those that resist this treatment need pass through the mill.

A common form of bolting machine consists of a frame shaped like a long hexagonal prism, which is rotatably mounted with its axis horizontal, and which is covered by fine silk gauze, e.g. Nos. 10–16 having 100–150 meshes to the linear inch. The sieve is surrounded by a closed casing having hopper-shaped outlets at the bottom by means of which the sifted starch can be filled into bags. Another form of bolting machine, the centrifugal bolter, not only sifts the starch, but breaks up soft lumps. It consists of a slowly rotating closed cylinder sieve covered with silk gauze, inside which a system of parallel laths, acting as beaters, revolves rapidly. The sieve is enclosed in a casing which may be provided at the bottom with a conveyor worm for the sifted starch or with outlets for bagging. A centrifugal bolting machine by Uhland is shown in Fig. 48.

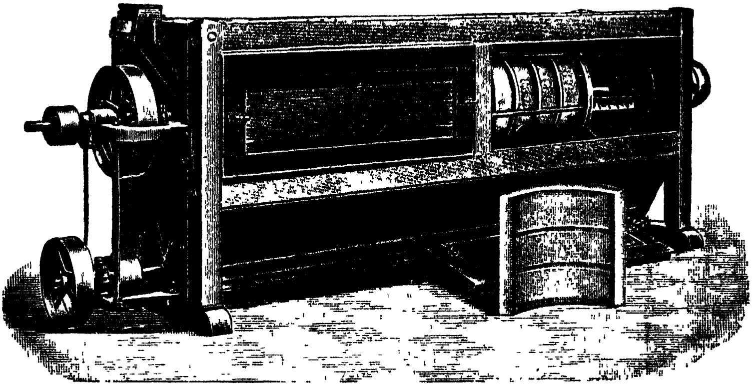


FIG. 48.

Centrifugal bolting machine by Uhland.

The powdering of lump starch is carried out in mills of special construction. Ordinary grinding mills are unsuitable because the frictional heat of the grinding surfaces would gelatinise some of the starch granules. One type of starch mill consists of a vertical cylindrical casing divided into three compartments by two perforated horizontal partitions. The upper partition has coarse perforations and upwardly projecting teeth like an ordinary grater. The lower one is a fine metal sieve. A vertical rotatory shaft extending centrally through the apparatus, has mounted on it in the top compartment radial blades or beaters, and in the middle compartment radial arms with brushes that sweep over the surface of the fine sieve. Dried starch fed into the top compartment is broken up by the beaters and the teeth of the upper partition until it is small enough to pass into the middle compartment, and there it is further comminuted by the brushes until it passes through the lower sieve into the bottom compartment, whence it is discharged. Another type of starch mill is the ball mill which consists of a slowly rotating inclined cylindrical drum, divided into compartments by transverse sieve partitions. A number of wooden balls in each compartment by their rolling and rubbing motion are the pulverising agents in this machine.

Fig. 49 shows a starch mill constructed by Uhland, working on the principle of rapidly revolving beaters which pass, with only a small clearance, between projections of complementary shape attached to the walls of the casing. The mill is fitted with interchangeable screens, the mesh of which determines the fineness of the milled starch.

## Factory Yields of Potato Starch.

The chief loss of starch in the factory is in the exhausted pulp. The latter always contains a certain amount of bound starch, enclosed in cells which the raspers and mills have failed to tear open, and no amount of washing of the pulp will extract this starch. Its amount depends on the efficiency of the rasping and milling operations. Under the best conditions it may be reduced to less than 1 per cent. of the weight of the potatoes worked, but it is usually more, and in some cases as high as 2 per cent. The exhausted pulp usually contains also some free starch which has escaped extraction on the washing sieves. This should not exceed 0·2 per cent. of the

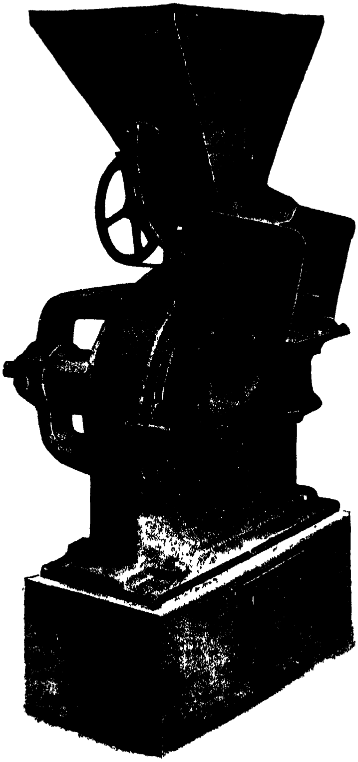


FIG. 49.

Starch mill by Uhland.

weight of the potatoes, but it is much more in some factories. Given moderately good working, the exhausted pulp may thus contain an amount of starch equal to 1·5–2 per cent. of the weight of the potatoes worked. Other factory losses are small in comparison. The yield of water-free starch is thus about 1·5–2 per cent. less than the actual percentage of starch in the potatoes, or about 3 per cent. less than their starch value as indicated by the potato-balance. It should be borne in mind, however, that 1 part of water-free starch corresponds to 1·25 parts of commercial starch, since the latter contains about 20 per cent. of moisture.

## THE FINAL PRODUCTS.

*Green Starch.*—This is manufactured as a final product in Germany chiefly by small factories, and its quality is commonly inferior to that of the dry starch produced by the larger factories. Its usual composition is, according to Saare:—moisture 47·9–51·5 per cent., starch 47·5–52·0 per cent., soluble matters 0·08–0·2 per cent., sand 0·03–1 per cent., fibre, etc., 0·01–0·3 per cent.

Green starch should be worked up as soon as possible after manufacture, as it does not keep well. It is used chiefly for the production of starch sugar or syrup, and to some extent for the manufacture of dextrin and "potato-sago." In rare cases the better grades are employed in the textile industry.

*Dry Starch.*—This is sold either in the form of lumps or as fine flour. In Germany, which is the chief centre of potato-starch manufacture, there are several generally recognised grades of quality. The Berlin and Hamburg markets have established certain standards to which first grade or *Prima* starch must conform. Products of lower quality are classed as *Secunda* or *Tertia*, but there are no definite standards for these. Many of the larger factories produce more than one quality of *Prima* starch, and market their best products under such names as *Superieur Prima*, *Hochfein Prima*, or *Extrafein Prima*. *Superieur Prima* has now become a recognised grade on the market.

According to the rules of the Berlin and Hamburg markets, *Prima starch* must be free from chlorine and technically free from acidity, and should contain not more than 20 per cent. of moisture. Moisture-contents between 20 and 22 per cent. involve certain deductions from the price paid for the starch, and starch containing more than 22 per cent. is not tenderable as *Prima.*

According to Saare, the best method of testing starch qualitatively for acidity is to spread out a small quantity of the sample and moisten it with 2–3 drops of a neutral solution of litmus which has been purified to increase its sensitiveness; if the starch is neutral the litmus will appear bluish or purple, whilst a red colour indicates acidity. The quantitative determination of the acidity of potato starch is in Germany carried out by mixing 25 grams of the starch with 25–30 c.c. of water, adding phenolphthalein, and titrating with $N/10$ sodium hydroxide solution. The sample is classed as faintly acid, acid, or strongly acid, according as the volume of alkali required is less than 5 c.c., between 5 and 8 c.c., or more than 8 c.c. A sample requiring less than 1·5 c.c. of $N/1$ sodium hydroxide solution per 100 grms. is regarded as technically free from acid, and may be graded as *Prima* starch, if satisfactory in other respects.

Apart from the definite standards already mentioned, custom requires that *Prima* starch should conform to a certain level of quality in respect of colour, lustre, taste, odour, and absence of sand and dark specks. The colour should be pure white, although sometimes a slight suspicion of blue or yellow is preferred. Potato starch has usually a faint characteristic odour, reminiscent of freshly cut potatoes, and attributed to the presence of minute quantities of ethereal oils, but it should be free from any musty, sour or putrid odour.

The lustre of potato starch depends on the size of the granules. The highest grades are the most lustrous and have the largest granules. This is well illustrated by the following figures published by Saare, and representing the average diameter (mean of length and breadth) of the granules of samples of various grades of potato starch:—Finest quality starch, 0·0355 mm.; superior *Prima* starch, 0·0328; second product *Prima* starch, 0·021; *Secunda* starch, 0·0169; *Tertia* starch, 0·0125 mm.

If the moisture-content of starch is reduced to 8–9 per cent. fissures are formed in many of the granules, and the lustre is impaired.

All commercial samples of potato starch contain dark specks visible to the naked eye. Most of these represent particles smaller than the largest starch granules. Their presence may be due to imperfect washing of the potatoes, to deposition of minute particles of coal or other foreign matters during manufacture, or to a variety of causes some of which are unavoidable. If present in large numbers they detract from the value of starch for the manufacture of dextrin or for paper dressing or colour printing. Saare has described a method by which the relative numbers of specks in different samples of starch may be compared. Each sample is spread out on paper, a sheet of glass is laid on it, and the number of dark specks per square decimetre, detectable by the naked eye, is counted. In the best qualities of *Prima* starch, Saare found less than 30 specks per sq. dm., in medium *Prima* samples 27–170, in inferior *Prima* samples 145–450, and in samples which would not be classed as *Prima* by experts on account of the large number of specks, 700–800.

The ash-content of *Prima* starch is usually 0·2–0·3 per cent., and should not exceed 0·5 per cent.

An important property of starch for technical purposes is its gelatinising power, as indicated by the strength or stiffness of the pastes which it forms with hot water. There is no generally recognised method of measuring this property quantitatively. Most users of starch to whom it is of importance, are satisfied to make comparisons between samples by preparing from them starch pastes of some standard concentration under strictly similar conditions, and judging the relative stiffness of the pastes by inspection or by some simple mechanical or technical tests. A very simple procedure employed in the laboratory of the German Starch Trade Institute is one proposed by Schreib, and carried out as follows:—4 grams of the starch sample is mixed with 50 c.c. of cold water in a small porcelain dish, and then heated to boiling, with constant stirring, over a Bunsen flame. As soon as the paste is transparent and begins to froth up, the flame is removed, but stirring is continued for some time longer. Boiling must not last more than one minute. A good starch should yield a paste which after cooling is too stiff to flow out of the dish.

There are no definite standards for the commercial valuation of the inferior grades of potato starch. They are usually sold on sample, regard being paid to colour, lustre, absence of specks, and taste. They are more or less acid in reaction, since acid is commonly used in their purification.

*Exhausted Pulp.*—This is a light yellowish or grey mass, usually containing over 90 per cent. of water. The dry matter contains as a rule about 40–70 per cent. of starch, 10–20 per cent. of fibre, 4–5 per cent. of protein, 0·2–0·5 per cent. of fat, and 4–8 per cent. of ash. It is usually employed for cattle feeding, but for this purpose it is improved by the removal of part of its water. One method of effecting this is to store the wet pulp in trenches in the ground; a large amount of its moisture drains away and an acid fermentation sets in, which, if it does not go too far, renders the pulp more palatable to cattle. Many factories employ pulp presses for expelling part of the water. In one type of press the pulp is forced up through a perforated cylinder against a weighted cover by means of a closely fitting, rotating worm. In another the wet pulp is pressed between perforated rollers. The expulsion of water is facilitated by adding to the wet pulp a small proportion of lime, which does not detract from its value as fodder. In this way it becomes possible to reduce the moisture-content of the pulp to about 75 per cent. or even less. In some factories the pulp is dried after as much moisture as possible has been removed by pressure. In the dried state the pulp will keep indefinitely.

# CHAPTER VII.

## MANUFACTURE OF WHEAT STARCH.

THE extraction of starch from wheat is the oldest of the starch industries. It was practised in ancient Greece, and probably a fermentation process was used, for the Greek name of the product, *αμυλον*, appears to signify that the starch, in contrast with ordinary wheat flour, was obtained without milling. In Western Europe, wheat starch is known to have been used for dressing linen as early as the sixteenth century. At the present time the annual production of wheat starch is small in comparison with that of maize- or potato starch, and probably less than that of rice starch. Germany and Czechoslovakia are the chief producing countries. The former, in 1925, had 17 factories manufacturing wheat starch, with a roughly estimated output of 29,000 tons.

The methods employed for extracting starch from potatoes are not directly applicable to wheat, owing to the wide differences in physical characters and chemical composition between the two materials. As will be explained later, the earlier methods of manufacturing wheat starch employed whole wheat grains as raw material, whilst the later methods substituted wheat flour. The average composition of whole wheat grains, as calculated by König from numerous published analytical data, is as follows:—moisture, 13·56 per cent.; proteins, 12·42 per cent. ; fat, 1·70 per cent.; starch, 64·07 per cent.; sugar, gums, etc., 3·82 per cent.; fibre, 2·62 per cent.; ash, 1·79 per cent. The composition of wheat flour differs from this in certain respects owing to the removal of most of the husk and a considerable portion of the fatty and mineral matter; the proportion of fibre may range between 0·1 and 1 per cent., that of fat between 0·5 and 1·5 per cent., and that of ash between 0·3 and 0·8 per cent., whilst the starch-content is usually between 65 and 70 per cent.

The chief difficulty in the manufacture of starch from wheat arises from the presence of a large proportion of gluten. This is a nitrogenous material of proteid nature and constitutes 80–90 per cent. of the total proteins of wheat or wheat flour. It swells in water without dissolving, and becomes soft and sticky, and in this condition it interferes with the washing-out of the starch from the disintegrated wheat. It is gluten that gives to dough made from wheat flour its characteristic plasticity. If a lump of dough is kneaded between the fingers in running water, the starch is slowly washed out, leaving the gluten as a soft, yellowish, sticky mass. Performed carefully over a fine sieve to catch any falling particles of gluten, this simple experiment can be used to determine quantitatively the gluten-content of samples of wheat flour. Gluten is not a single substance, but a mixture of two wheat proteins, gliadin and glutenin; and obtained as described above it is usually contaminated with small quantities of other constituents of the wheat grain.

The various methods of manufacturing wheat starch differ chiefly in the processes employed for obtaining the raw starch; in respect of the purification of the starch they have much in common. The oldest method for extracting the starch is the so-called Halle or Fermentation Process, in which the grain, softened by steeping in water, is crushed between rollers, and then made into a mash with water and allowed to ferment for a week or two. This so modifies the properties of the gluten that it no longer interferes seriously with the washing-out of the starch. A second method, known as the Alsatian Process, consists in steeping and grinding the grain and washing-out the starch without previous fermentation. A third method, Martin's Process, which is now the most important one, employs wheat flour instead of whole wheat, and is essentially a large-scale adaptation of the experiment described above in which the starch and gluten are separated by kneading dough in water. Another method which employs wheat flour as raw material is Fesca's Thin-Mash Process. In this, the flour is not formed into dough, but is mixed with water, and at once treated in a centrifuge to separate the starch from the other constituents of the flour. In the following section these four methods of extracting wheat starch will be described, and the purification of the raw starch will be dealt with afterwards.

## EXTRACTION OF THE RAW STARCH.

*Halle or Fermentation Process.*—The wheat is steeped in water until the grains are soft enough to be crushed between the fingers. This requires about 3–4 days in summer and two or three times as long in very cold weather. The steeping takes place in vats of wood or masonry, or most conveniently in hopper-bottomed tanks. The water is changed from time to time. When sufficiently softened the wheat is allowed to drain, and then crushed between rollers, but not finely ground. It is next transferred to a fermentation vat and mixed with water to form a mash which is allowed to undergo spontaneous fermentation. A considerable amount of time can be saved, especially in winter, by adding sour liquor from a previous fermentation, or sour dough, to start the mash fermenting. At a temperature of about 25° C. the fermentation is completed within a week, and at 15° C. within a fortnight. During the early stages, alcoholic fermentation occurs with brisk evolution of gas. Later, the mash becomes acid owing to acetic, lactic and butyric ferments, a mould flora extends over the surface, and putrefaction sets in producing a very offensive odour. When this stage has arrived, and the initial evolution of gas has entirely ceased, the process is stopped. If it is carried too far, the liquid portion of the mash begins to become viscous. The fermentation process, conducted as described, weakens the cellular tissue of the wheat, and softens and partially dissolves the gluten to such an extent that the starch can be washed out without difficulty.

In a modified form of the fermentation process, the wheat, without steeping, is ground or crushed in stone mills or roller mills, and then sent directly into the fermentation vat. This method of working saves time, since steeping and fermentation proceed simultaneously, but the grinding of the dry wheat, especially between mill-stones, is apt to disintegrate the husks to an undesirable extent and render the purification of the starch more difficult.

After the fermentation is complete the yellow, sour liquor is drained off from the mash, and the residue is washed to extract the starch. This is usually effected in a large closed washing drum, mounted to rotate slowly with its axis horizontal. The cylindrical surface of the drum may be formed of finely perforated sheet metal, or of cloth stretched over wooden cross-pieces which join the two end-plates of the drum. After the drum has been half filled with mash, it is set slowly revolving, water is introduced by a pipe passing through the bearings, and the starch milk which escapes through the perforated walls is collected in a trough beneath the drum. About an hour is required for washing each charge, representing about ½–1 ton of mash.

The fermentation process gives a good yield of starch, usually 50–60 parts of commercial starch per 100 parts of wheat, but it has very serious disadvantages in comparison with more recent processes. It occupies a long time from start to finish, the fermenting mash and the liquors and factory effluents derived from it have a very obnoxious odour, and the process does not enable the gluten of the wheat to be recovered in a commercial form. The exhausted residues from the washing drum consist of wheat husks, germs and "sour gluten," but these residues are only suitable for pig fodder For these reasons, the Halle process is scarcely if at all employed at the present time.

*Alsatian or Hungarian Process.*—This was during the first half of the nineteenth century the only competitor of the Halle Process. It is still used, but not to the same extent as the Martin Process, which will be described next. It differs from the Halle Process by the omission of fermentation, and this omission renders difficult the washing-out of the starch from the disintegrated wheat.

The wheat is steeped in the same manner as for the fermentation process. The steeping tends to impair to some extent the adhesive properties of the gluten in the grain, and for this reason Rehwald recommends that it should be hastened by maintaining a temperature of about 30° C. when gluten is to be recovered in a commercial form. The steep water must be changed often enough to prevent development of acidity.

The steeped wheat is ground between mill-stones or rollers, preferably between channelled rollers so that the soft starchy contents of the grains are squeezed out and crushed without unnecessary disintegration of the husks. In the subsequent washing-out of the starch the gluten particles unite and form lumps which enclose starch, and therefore require thorough kneading. At one time the washing-out of the starch was effected by tying up the crushed wheat in cloth sacks and treading it in water. A modern form of extractor consists of a finely perforated trough in which the crushed wheat is thoroughly stirred and kneaded by arms rotating on a horizontal shaft which extends through the trough. A sprinkler pipe above the trough provides a continuous supply of water, and the starch washed out escapes into a collecting trough surrounding the perforated one. In this apparatus, about an hour is required to wash out the starch from a 2 cwt. charge of wheat.

Another method of operating is to combine the crushing of the wheat with the extraction of the starch. If roller crushers are used, there should be several pairs, one above another, with water sprinklers, and a sieve below to collect the mixture of husks and gluten, which should be passed through the roller system a second time.

The raw starch milk washed out from the crushed wheat is passed through shaking sieves of silk gauze, and the starch is deposited in vats or centrifuges or on tables, and further purified. The Alsatian Process yields about 35–45 parts of first grade commercial starch, and 10–20 parts of second grade per 100 parts of wheat. The residue left in the extractor consists of wheat germs and husks, together with gluten. This forms an excellent feeding stuff. If it is desired to recover the gluten, the mixture must undergo a long washing process combined with kneading, as the husks are difficult to wash out. Apparatus employed for this purpose consists of a perforated washing drum with projections inside which serve to tear the lumps of gluten as the drum revolves. A large amount of gluten is lost, however, in this washing process, being carried away in small particles with the husks; in consequence, the yield of dry gluten obtained finally is usually not more than 5–6 per cent. of the original wheat.

*Martin's Process.*—This process, which employs wheat flour instead of whole wheat, was first proposed by Martin, of Paris, in 1835. It was not until some decades later that it began to be widely used, but by the end of the nineteenth century it had assumed the first place among methods of wheat starch manufacture. Although employing a more costly raw material than the Alsatian process, it dispenses with a number of operations necessary to the latter and works with a much cheaper plant. Since its raw material is already free from husks, it is able to produce a good yield of technically pure gluten by a single washing-out operation.

The wheat flour is first worked to a dough with 40 per cent. of its weight of water, in a doughing machine such as is used in steam bakeries. The dough is left to stand for about an hour to allow the gluten to swell, and is then transferred in lumps weighing several pounds to the washing-out machine. A modern type of machine for this purpose consists of a horizontal grooved roller suspended from overhead bearings, which by a to-and-fro motion, repeatedly rolls out and turns over the dough on a fixed grooved bed flanked by sieve surfaces. As all parts of the dough are thus in turn worked to the surface, the starch is washed out by jets of water from an overhead sprinkling pipe, and carried through the sieve surfaces to a collecting trough. In an older type of machine the dough is continuously rolled between parallel rubbing surfaces made of strong wire gauze covered with cloth, one surface moving backwards and forwards over the other whilst water plays on it and washes the starch through the cloth and the sieve surface.

The gluten which remains in the extraction apparatus after the starch has been washed out is a soft yellow or greyish mass. In the air-dry state, containing about 8–10 per cent. of moisture, it amounts to 10–15 per cent. of the weight of the original flour, and represents a valuable product commanding a higher price than the starch itself. The yield of starch obtained per 100 parts of flour is 45–55 parts of first grade product and 12–20 parts of an inferior or glutinous starch. It is a disadvantage of Martin's process that a considerable portion of the starch is contaminated with finely divided gluten, from which it cannot be separated by ordinary methods of purification, and this accounts for the relatively large proportion of inferior starch which the process yields. Special methods proposed for overcoming this difficulty will be mentioned in the section on the purification of wheat starch.

*Fesca's Thin-Mash Process.*—In this process, wheat flour is employed as raw material, but instead of being worked into dough, it is mixed with sufficient water to form a thin paste or mash, and then spun in a centrifuge having a non-perforated drum. The starch granules, being denser than the other suspended matters present, are deposited first against the walls of the drum; and the gluten, which is in a finely divided condition, in part remains in suspension in the liquid, and in part is deposited as a softer layer on the compact starch layer. This process extracts the raw starch in a much shorter time than any of the others, with the minimum of plant and the minimum of water. The liquor discharged from the centrifuge after the deposition of the starch, contains, besides some fine starch and most of the gluten, all the other non-starchy constituents of the flour, insoluble and soluble. The liquor is, therefore, very suitable for incorporation in feeding stuffs, and this is the usual method of disposing of it, either in its original condition or after evaporation. According to Fesca, this process will yield from 100 parts of flour, 40 parts of commercial starch and 54 parts of air-dry nutritive meal containing 22 per cent. of protein and 67 per cent. of starch and other solids. The chief disadvantage of Fesca's process is that it leaves the gluten in a condition suitable only for nutritive uses. Most wheat starch manufacturers still adhere to Martin's process, because it yields substantially pure gluten suitable for either nutritive or technical purposes.

According to J. Keil,[1] the liquid slop discharged from the centrifuge in Fesca's process is not concentrated enough to be well suited for incorporation in foodstuffs for human beings. He therefore proposed a process in which wheat flour is kneaded with about its own weight of water containing 0·2 per cent. of hydrated lime. The kneading is continued for 30–45 minutes, by which time the flour and water form a thick half-liquid mass, which is then introduced into the centrifuge. The starch separates well, leaving the gluten as a very soft mass containing all the non-starchy matters of the flour and suitable for use in the preparation of noodles or bake-house products. On the ground that the use of lime reduces the nutritive value of the gluten by splitting off lecithin and destroying enzymes, Klopfer[2] has proposed to employ a 1 per cent. solution of sodium bicarbonate, which produces a clean separation of starch in the centrifuge. In a later process, Klopfer[3] makes use of a 1 per cent. solution of common salt and still later he employs enzyme preparations and extracts of green malt.[4]

## PURIFICATION OF WHEAT STARCH.

The mechanical operations employed in the purification of the raw wheat starch extracted by the processes described in the preceding section, are similar to those employed in the treatment of potato starch, and comprise washing with water, passing through sieves, and depositing in vats, on tables or in centrifuges. The very small size of wheat starch granules as compared with those of potato starch, however, and the presence of finely divided gluten in raw wheat starch, are responsible for certain differences in procedure in the two cases.

The sieves employed in the purification of wheat starch are usually shaking sieves fitted with silk gauze, the mesh of

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[1] G.P. 102,465.

[2] G.P. 201,969.

[3] E.P. 11,159 of 1907.

[4] E.P. 19,726 of 1908.

which depends on the state of purity of the starch. The small size of wheat starch granules renders sedimentation in vats or on tables slower than that of potato starch; for complete deposition in vats one or two days may be necessary, and on tables the rate of flow of the starch milk must be much slower than is customary with potato starch. Centrifuges are extensively used in wheat starch factories. Those with perforated drums lined with cloth are suitable only for fairly pure wheat starch, for the glutinous matter in the raw starch rapidly chokes the pores of the cloth. Such centrifuges are therefore chiefly used for the final draining of the purified starch prior to drying, unless the starch is to be dried in blocks for the production of crystal starch, and then the draining is best carried out in box moulds. For the centrifugal treatment of raw wheat starch it is customary to use centrifuges with imperforate drums like those employed in Fesca's Thin-Mash Process. The raw starch is fed to the centrifuge as a suspension of about 22° Baumé. Rotation causes the deposition of a compact layer of comparatively pure white starch against the walls of the drum, and inside this is deposited a layer of more or less coloured glutinous starch, whilst the liquid containing the lightest and finest particles in suspension forms the innermost stratum. After the drum has been brought to rest the liquid is drawn off, and the soft layer of glutinous starch is removed from the surface of the main starch layer by careful scraping. In some cases the scraping is effected by means of a blade specially mounted on the spindle of the drum so that it trims the starch cake in an even circular path at an adjustable distance from the centre of the drum. Sometimes at this stage a further charge of raw starch milk is spun in the drum without removal of the pure starch layer previously deposited, so as to obtain a thicker cake before removing it.

*Treatment of Glutinous Starch.*—By whatever method the deposition of raw wheat starch is effected, whether in vats or centrifuges or on tables, there is always obtained a larger or smaller amount of somewhat discoloured glutinous starch, which deposits more slowly than the purer fraction, and forms a softer and less compact layer. Repeated sedimentation of this impure starch may yield a certain amount of pure starch, but there remains a fraction which resists purification by ordinary methods. It consists very largely of the smaller starch granules associated with a small proportion of fine gluten. In Martin's process as much as 25 per cent. of the total starch may be obtained in this condition. In some cases it is dried and sold as an inferior grade of starch. For this purpose it must be collected in filter presses, since in vats or centrifuges it does not form a cake compact enough for drying. The filter press cakes are broken up and dried at temperatures rising from 30° to 60–70° C. The product has a brownish colour and finds a limited use for low-grade textile work and also as an adhesive in cases where a colourless product is not required.

Various methods have been proposed for the recovery of pure starch from glutinous starch, or for reducing the yield of the latter in favour of the first product. For the latter purpose the raw starch milk is in some factories subjected to a fermentation process. More frequently the glutinous starch alone is subjected to fermentation. The fermentation is either allowed to start spontaneously, in which case it may occupy a week or two, or it is hastened by addition of "sour liquor" from a similar operation. The result of fermentation is to effect a partial degradation or dissolution of the gluten whereby it becomes more easily separated from the starch by washing and sedimentation.

Chemical agents such as ammonia and acetic acid have been used for the treatment of glutinous starch. Acetic acid at a concentration of 1 per cent. has a distinct solvent action on gluten, and possibly the beneficial effect of fermentation on the purification of starch is largely due to the acetic acid formed. Both ammonia and acetic acid are volatile, and therefore any traces remaining in the purified starch would probably evaporate during the drying process. In this respect acetic acid is preferable to sulphuric acid, which is difficult to wash out of the starch completely and is non-volatile at the drying temperature. According to Martin, almost the whole of the starch extracted from flour by his process can be recovered as first-grade product by adding sufficient caustic soda to the raw starch milk to render this alkaline to litmus paper, after which the alkaline milk is allowed to stand for 2 hours and then passed through a fine hair sieve with 200 meshes to the linear inch. The use of caustic soda in the treatment of starch requires caution. Only very dilute solutions should be used. At 2 per cent concentration caustic soda transforms the starch instantaneously into a gelatinous mass.

## DRYING OF WHEAT STARCH.

The drying of wheat starch, like that of potato- and other starches, must be carried out at a low temperature until most of the moisture has been removed, in order to avoid gelatinisation. Preparatory to drying, the starch may be drained in a centrifuge to remove as much water as possible, unless the dried product is required in blocks or as "crystal starch," in which case the draining is usually best carried out in special draining moulds similar to those employed for rice starch (see p. 172). The further operations involved in the production of "crystal starch" are also substantially the same as in the case of rice starch. A trace of gluten remaining in wheat starch after the purification processes is believed to improve the coherent quality of the dried starch, and thus to facilitate the production of "crystals" which do not readily fall to pieces. In very white starch, from which the gluten has been eliminated as completely as possible for the sake of the colour, the necessary cohesion is sometimes imparted by adding a small quantity of liquefied starch or colourless dextrin.

## THE FINAL PRODUCT.

Commercial wheat starch usually contains less moisture than potato starch, the average proportion being 11–15 per cent. Good white samples contain as a rule less than 0·5 per cent. of protein and about 0·15 per cent. of fat and 0·25 per cent. of mineral matter. These values may be considerably exceeded in yellowish samples such as the scrapings obtained from the partially dried blocks in the production of "crystal starch."

According to Saare, the manner in which lump starch breaks up in cold water is indicative of its quality. If a piece of starch is placed in a saucer and half covered with water, and the saucer is rocked from side to side, starch of good quality soon breaks up and forms a perfectly uniform suspension in which no lumps can be detected, whilst inferior products usually leave a number of small lumps or knots.

## WHEAT GLUTEN.

The gluten obtained as a by-product of wheat starch manufacture is of proteid nature, and consists essentially of glutenin and gliadin, but it usually contains small quantities of other constituents of the wheat and a considerable amount of starch which not infrequently exceeds 10 per cent. of the total dry matter. In the fresh state, as obtained from dough, it forms a soft yellowish mass, elastic and very extensible, and tenaciously adhesive to dry surfaces. In this state, after being squeezed in the hand and drained to remove excess of water, it usually contains 30–70 per cent. of moisture. When completely dried it forms a brown or yellowish horny material

Gluten is insoluble in water, but soluble in dilute acids and caustic alkalis. It dissolves slowly even in comparatively weak acids, e.g. acetic acid at 1–3 per cent. concentration. Its elastic and adhesive character is impaired by prolonged contact with cold water, and much more rapidly in hot water. The incorporation of fresh gluten in fodders and foodstuffs, which would be difficult at the ordinary temperature, can thus be effected by heating.

The amount and quality of gluten obtained in the various processes of wheat starch extraction are very widely different. The fermentation process yields a very small amount of sour gluten (about a quarter of that originally contained in the wheat), mixed with wheat germs and husks and fit only for fodder. The Alsatian process yields in the first place a mixture of sweet gluten with germs and husks, which, after heating to distribute the gluten, makes an excellent fodder. To obtain pure gluten from it a prolonged washing and kneading operation is necessary. The Martin process for the manufacture of starch from wheat flour is the process at present employed by most of the larger factories and is the main source of the gluten employed for technical purposes; it yields about 8–15 per cent. of gluten substantially free from foreign matters except starch. The Fesca process, in which wheat flour is mashed and centrifuged without doughing and kneading, yields the gluten in the form of an aqueous suspension containing all the non-starchy matters of the flour besides a considerable amount of starch. It is therefore better suited for nutritive than for technical purposes.

The chief applications of gluten are as an adjunct to fodders and foodstuffs, as an adhesive, and as a thickening agent in textile printing.

Gluten cannot be kept for long in the moist state; it begins to turn sour after 24–36 hours in warm weather or 2–3 days in cold weather. When it is intended for foddering purposes, a moderate amount of sourness is not detrimental, but renders the gluten more palatable. It is usually heated, together with other waste factory products, such as starch sludges from which no more starch can be recovered; the gelatinisation of the starch granules contained in the gluten loosens its compact texture and renders it more easily digestible.

For human alimentation, gluten is an important item in diabetic dietaries, and is added to dough in the making of baked foods of various kinds. A mixture of one-third of gluten to two-thirds of ordinary dough serves for the preparation of such foods as noodles and macaroni. A smaller proportion added to dough for bread is said to improve very considerably the appearance and flavour of the latter as well as its nutritive value. The gluten paste produced by the various forms of Fesca's process of extracting starch from flour is particularly well suited for such uses, for it contains all the non-starchy nutriment of the original flour.

A method of drying gluten invented by Hundhausen consists in spreading thin layers of it on revolving rollers which travel on endless chains through a drying chamber. The dried material separates from the rollers in flakes, which are afterwards ground to powder. The yellow product, known as "Aleuronat," is used as a basis for diabetic pastry and as an adjunct to foodstuffs in various ways. The limits of composition of eight samples of such dried gluten, recorded by König, are as follows:—moisture, 7·95–10·96 per cent.; protein, 69·07–86·35 per cent.; fat, 0·24–2·29 per cent.; ash, 0·81–1·49 per cent.; starch and other matters, 8·13–17·68 per cent.

For use as an adhesive and thickening agent gluten is subjected to a fermentation process. According to Wagner, if it is kept at 15–18° C. for 7–8 days it becomes acid and softens to a mass of almost syrupy consistency. In this condition it may be thinned with water and spread with a brush. It forms in fact a size of inoffensive odour and can be kept for 8–10 days without decomposition. It serves as a substitute for egg-white and glue in colour-printing on fabrics, and can be dried and stored for indefinite periods. The precise conditions of fermentation employed in practice are not made public, but the liquefied product is spread on greased plates in a thin layer and dried at a comparatively low temperature. The dried flakes thus produced are known as Vienna Size or Shoe-makers' Paste.

# CHAPTER VIII.

## MANUFACTURE OF MAIZE STARCH.

THE maize starch industry dates from the middle of last century, but in the United States of America it has attained such dimensions as to rival or surpass in importance the European potato starch industry. The output of the United States in 1900 was 110,292 tons, but by 1923 it had increased to 374,688 tons. The importance of the industry may be judged from the fact that the output of starch for 1923, as given above, was valued at 29 million dollars, and there are also important by-products in the form of maize oil, oil cake and other feeding stuffs. In the same year there was produced more than 200,000 tons of starch glucose valued at 16 million dollars, and a quantity of syrup products valued at 33 million dollars.

Maize starch is manufactured in various other countries, but in small quantities compared with the output of the United States. Germany is said to have twenty factories, with an estimated production of about 10,000 tons. Canada has several factories, and produced about 8000 tons in 1918. Great Britain has several maize starch factories, but imports very large amounts, chiefly from the United States; more than 80,000 tons were imported from this source in 1924 and nearly 60,000 tons in 1923.

The grain of maize (*Zea mais*), or corn as it is termed in America, differs from that of wheat not only in size but also in composition and in the distribution of the various constituents, and in consequence the methods employed in extracting the starch are not the same in the two cases. The maize grain consists of an outer hard integument or husk, a starchy endosperm, and an embryo or germ. The germ is easily detached after the grain has been softened by steeping in water. The relative weights and composition of the parts of the maize grain are shown in Table VI, published by T. B. Wagner.[1] It is clear from this table that the germ, which only amounts to about one-tenth of the total grain, contains most of the mineral matter and by far the greater part of the oily or fatty matter of the grain. The endosperm or starchy portion of the grain contains about 11 per cent. of nitrogenous or glutinous matters, which are mainly concentrated in a hard, yellow peripheral part of the endosperm consisting of so-called gluten cells. The gluten contained in these cells, unlike that of the wheat grain, cannot be obtained in a coherent dough-like mass; it remains finely divided and renders difficult the purification of the starch. The figures representing nitrogen-free extractives include starch, sugar, gums, etc., and like all the other figures in the table are calculated on dry substance. The moisture-content of maize is about 9–14 per cent. and the starch-content about 60–65 per cent. Substantially the whole of the starch is contained in the endosperm portion of the grain.

### TABLE VI.

PERCENTAGE COMPOSITION OF THE DRY SUBSTANCE OF THE PARTS OF THE MAIZE GRAIN.

| | Proportion of parts. | Ash. | Protein. | Fibre. | Nitrogen-free extractives. | Fat. |
|---|---|---|---|---|---|---|
| Whole grain .. | 100·0 | 1·7 | 12·6 | 2·0 | 79·4 | 4·3 |
| Skin .. .. | 5·5 | 1·3 | 6·6 | 16·4 | 74·1 | 1·6 |
| Germ .. .. | 10·2 | 11·1 | 21·7 | 2·9 | 34·7 | 29·6 |
| Endosperm .. | 84·3 | 0·7 | 12·2 | 0·6 | 85·0 | 1·5 |

In the manufacture of starch from maize it is the general practice to soften the grain thoroughly in warm water containing either a small quantity of sulphurous acid or calcium bisulphite. The next operation is milling, and in this certain

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[1] *J. Soc. Chem. Ind.*, 1909, 343.

differences in procedure arise. In some processes, more particularly the older ones, the grain is ground as a whole, although usually with as little disintegration of the husk and embryo as possible. The starch is then washed out, leaving a residue, which is sometimes further ground and washed. A more modern method of operating is to split or partially crush the steeped maize sufficiently to enable the embryo or germ to be separated from the rest of the grain, and, after this separation has been effected by flotation, to grind the rest of the grain thoroughly in stone mills and then wash out the starch. The separation of the embryo not only enables the oil in it to be conveniently recovered as a by-product, but also prevents the oil from contaminating the starch and rendering the purification of the latter more difficult.

The mechanical operations employed for the purification of maize starch are in general similar to those used with other starches, but in many cases their effect is enhanced by the use of small quantities of certain chemical agents, usually either sulphurous acid or caustic soda, added to the starch milk in the course of purification. There are generally supposed to be slight differences in the properties of the final starch according as sulphurous acid or caustic soda is employed, the acid starch being somewhat finer in colour but not so thick-boiling. Acid starch is largely used in the moist state, for the manufacture of starch sugar and syrup, whilst alkaline starch is more usually employed for laundry work. Some factories produce both acid and alkaline starches. Below are given some details of the manufacture of maize starch without separation of the embryos, described by Archbold,[1] and following that is the more modern procedure with separation of the embryos.

## ALKALINE PROCESS WITHOUT SEPARATION OF THE EMBRYO.

The maize, after being steeped for three days at 60° C. in water, to which calcium bisulphite equivalent to 0·3 per cent. of sulphur dioxide has been added, is ground with a small quantity of water, and the thick magma thus produced is

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[1] *J. Soc. Chem. Ind.*, 1902, 4.

washed on shaking sieves. The residue retained by the sieves is again passed through the mills and again washed. The combined raw starch milks obtained from the first and second mill products are concentrated to a solid-content of about 13 per cent. by sedimentation in hopper-bottomed tanks and then drawn off into an alkali tank and treated with about 0·15 per cent. of caustic soda. This neutralises the acidity of the liquor and facilitates the subsequent separation of oily and glutinous impurities from the starch. The alkaline starch milk, after being diluted to 3–3½° Baumé, is allowed to flow over the starch tables, on which the raw starch is deposited, the liquor leaving the tables with a solid-content of little more than one per cent., of which one quarter is oil. The raw starch from the tables, containing about 0·1 per cent. of caustic soda, is conveyed to mixing vats, in which it is diluted to 11–12° Baumé, and then it is passed through fine shaking sieves which retain a considerable amount of impurity. The starch milk from the sieves is run into the washing vats, where it is allowed to deposit. Preparatory to draining and drying, the starch deposit is mixed with fresh water and sufficient caustic soda solution is added to raise its alkalinity to 0·1 per cent. The alkalinity gradually diminishes owing to the activity of acid-forming organisms, and when the thick starch suspension, containing about 70 per cent. of water, is run into the draining boxes or moulds, the alkalinity is about 0·075 per cent. After draining overnight the moisture-content is reduced to about 55 per cent. and the starch is turned out in blocks and allowed to drain further on tiles until the moisture-content is about 40–45 per cent. The blocks are then placed for 12 hours in a crusting kiln, in which the surface layers become discoloured, as described in the chapter on rice starch. After the discoloured layers have been scraped away, the blocks are wrapped in paper and returned to the kiln for the final drying. The scrapings from the blocks are usually mixed with water, treated with caustic soda, passed through sieves and re-deposited on tables.

Twenty years ago Archbold described this process as being largely used in America. Recent practice, however, favours the use of sulphur dioxide in the steep, and the separation of the maize embryo before the final milling of the grain. Purification by means of alkali is not so important a feature as in the process just described, and is often omitted altogether. For many of the details of this method of working, as described below, the authors are indebted to an interesting paper by W. P. Kaufmann.[1]

### PROCESS WITH SEPARATION OF THE EMBRYO.

*Extraction of the Raw Starch.*—The maize is steeped for 2–4 days in warm water, usually between 40° and 60° C. To repress the development of micro-organisms and to assist the swelling of the grain, it is usual to add about 0·3 per cent. of sulphur dioxide to the water, but this is sometimes postponed until one or two changes of plain water have removed most of the dirt and easily soluble matters from the outside of the grains. Steeping is usually carried out in large hopper-bottomed tanks having a capacity of 1000–2000 bushels of grain. Processes have been patented for carrying out the steeping in a battery of vessels worked in circuit, the liquor being passed through all in succession and replenished with sulphur dioxide as required. The individual vessels are cut out of circuit in rotation as their charges are fully steeped, and inserted again when re-charged with fresh grain.

The steeped maize is passed between rollers, which split and partially crush the grains without grinding them. In this way a large proportion of the starch is set free, whilst the germs or embryos are detached from the rest of the grains, but not disintegrated to any considerable extent. In America, mills of the Foos type are commonly used for this operation.

The next step is the separation of the germs from the rest of the grains. This is effected by flotation. The crushed or split grain from the mills is passed through "separators" or "degerminators," in which it is stirred up in water. A large proportion of the starch at once forms a milky suspension in the water, raising the specific gravity of the liquor as a whole. The germs or embryos part from the rest of the grains and,

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[1] *J. Soc. Chem. Ind.*, 1910, 527.

being rich in oil, and therefore light in density, rise to the surface of the starchy liquid, whilst the other portions of the grain fall to the bottom. The separator is usually a trough-shaped vessel with a stirring mechanism below the surface of the liquid and with paddles moving across the surface to skim off the floating germs. In one form of apparatus the trough is of V-shaped cross-section, and has a screw conveyor along the bottom which serves the double purpose of transporting the material through the trough and continuously stirring it, so that the germs have opportunity for escaping from the heavier maize residues. These separators operate continuously.

The embryos which are skimmed off from the top of the separator are washed on copper screens to remove adhering starch and are then dried. The moisture-content is first reduced to about 60 per cent. by squeezing out water in an extractor, and finally to about 4 per cent. by drying. The dried embryos are ground in a roller mill and conveyed to an oil extractor. Hydraulic presses are often used for extracting the oil, but there are more modern types of apparatus which operate continuously and yield oil of better quality. Maize oil is employed in large quantities in soap making, and to a smaller extent in tanning and in the preparation of certain paints and varnishes. Very large quantities are exported from America to European countries.

The cake from which the oil has been expressed is known as Maize Germ Cake and is a valuable feeding stuff; it contains about 21 per cent. of protein and 13 per cent. of oil.

The starch liquor from the separator or degerminator is passed through a shaking sieve and the coarse solid matter from the separator, representing the grains from which the germs have been separated, is ground thoroughly in stone mills. The ground product is pumped to feeding boxes, which deliver it to shaking sieves of fairly coarse silk gauze, e.g. No. 9 (with 90 meshes to the linear inch). The residue which does not pass through the sieve is thoroughly stirred up again with water and passed again over silk sieves to recover all possible starch from it. The final residue contains the bran and a large amount of glutinous matters of the original maize; it is freed from water as completely as possible in presses, and it may be employed as cattle food without further drying, or it may be dried and sold as Corn Bran, containing about 10 per cent. of protein and 2·7 per cent. of oil.

*Purification of the Raw Starch.*—The combined starchy liquors from the various sieves, known as Mill Liquor or Crude Starch Liquor, may be passed over another series of shaking sieves of fine silk gauze, e.g. No. 17 (with 160 meshes to the linear inch) by which a certain amount of fibrous and glutinous matter is retained. The liquor which passes through the sieves is concentrated to the right consistency by deposition and then allowed to flow over the depositing tables or runs, which are about 120 feet long, 1–2 feet wide and 6–8 inches deep, with a fall of 4 inches between the ends. The liquors which flow away from the lower end of the table contain fibrous and glutinous suspended matters together with about an equal quantity of starch which, however, is not economically recoverable as commercial starch. These liquors or "tailings" are passed through continuous settling tanks in which the suspended matters are separated as a sludge known as "slop" or "swill." The "slop" is often fed to cattle directly, but it is usually dried For this purpose it is passed into filter presses, which yield a cake containing about 60 per cent. of moisture, and the cake is then dried. One form of drying apparatus employed for this purpose consists of a slightly inclined rotatory cylinder, about 25 feet long, through which bundles of steam tubes extend. The inclination of the cylinder causes the material to travel from end to end, and a fan produces a current of air in the opposite direction. The material leaves the apparatus with only 10 per cent. of moisture, and it is then ground in a mill and bagged as Gluten Meal, containing about 31 per cent. of protein and 2·3 per cent. of oil. Very often the moist gluten meal is mixed with a certain proportion of corn bran (see above), and the mixture is dried and sold as Gluten Feed, containing about 23 per cent. of protein, and 2 per cent. of oil.

The deposit of "green starch" remaining on the tables contains about 50 per cent. of moisture and 0·5 per cent. of protein.

Without further purification it may be employed for the manufacture of glucose or starch syrup. When dried starch is required, the deposition on tables is repeated, with or without a treatment with alkali. A second tabling without any special treatment will reduce the protein-content of the starch from 0·5 to 0·3 per cent. A still purer and whiter product is obtained by treatment with very dilute caustic soda before re-tabling; the caustic soda causes the gluten to swell, and saponifies traces of oil in the starch, with the result that these impurities are more easily and completely eliminated when the starch is re-deposited on the tables.

A recently patented method[1] for the purification of raw starch depends on the fact that if air is blown through a suspension of the starch, a froth is formed which contains a much higher ratio of gluten to starch than the suspension itself. The longer the froth persists, the higher does this ratio become, because much of the starch drains out of the bubbles, whilst the greater part of the gluten remains. The permanence of the froth depends, in fact, on the presence of gluten, for suspensions of pure starch do not form a lasting froth. The patented process consists in blowing a copious froth on raw starch milk, allowing the froth to remain over a draining surface until it has lost most of its starch, and then sweeping it away into a separate vessel. It is claimed that by this process starch containing not more than 0·3 per cent. of gluten can be obtained without purification by tabling, and that the separated gluten recovered from the froth does not contain more than 10 per cent. of starch.

*Drying the Starch.*—The starch from the tables, mixed with sufficient water to form a thick paste of about 22° Baumé, is pumped into perforated cloth-lined moulding boxes and drained to a moisture-content of 44–45 per cent. It is then "broken out" in cubes of about 7–8 inches edge, which may be drained on tiles to lower the moisture-content by a few per cent. The blocks are next warmed in the crusting kilns, where sweating occurs, and the surface becomes brownish and then dries to a hard crust about $\frac{1}{8}$–$\frac{1}{4}$ inch thick. After the crust

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[1] E.P. 159, 838; 1921.

has been scraped off, the blocks contain about 28–30 per cent. of moisture. If "crystal starch" is required, the blocks are wrapped in paper for the final drying, but in other cases they may be broken up into large or small lumps, or into small fragments if powdered starch is required.

*Thick-boiling and Thin-boiling Starches.*—Starch made as described above, whether it has received alkaline treatment or not, is called thick-boiling starch, because in boiling water it yields very viscous pastes which on cooling set to more or less stiff jellies that break with a vitreous fracture. Thick-boiling starches in fact possess, almost unimpaired, the properties of starch in its natural condition. It is said that the high temperature employed in the steeping of maize, and the presence of sulphur dioxide, are responsible for a certain loss of viscosity of the starch in the gelatinised condition, and purification by alkali is said also to have a similar effect; but these losses of gelatinising power are slight in comparison with those which are intentionally brought about in the manufacture of the so-called thin-boiling starches. In America, thick-boiling starches are classified as "chemicalled" or "unchemicalled"; the latter are those purified without alkali or other chemical, whilst the chemicalled starches comprise those treated with alkali. Thick-boiling laundry starches are usually chemicalled, but unchemicalled starches are used for baking powders and culinary purposes, and also for certain textile applications. The production of thin-boiling starches consists in "modifying" or partially hydrolysing the starch, usually by means of acid. According to the extent of the modifying treatment, the starch yields pastes of greatly reduced viscosity, which are extensively used in laundry work, as they penetrate into the interstices of the fabrics much more readily than pastes of thick-boiling starches. The modification may be effected by making a thick suspension of the purified starch in water and adding a small quantity of hydrochloric or sulphuric acid. The suspension may then be gently heated below the temperature of gelatinisation, to produce the necessary degree of modification, and afterwards washed and dried. Or it may be drained, and the starch dried with the acid in it, so that modification occurs during the drying process.

## COMMERCIAL MAIZE STARCH.

The quality of maize starch depends to some extent on the methods of manufacture employed. The thick- or thin-boiling character of the starch is decidedly dependent on its treatment in the factory, as already explained. In respect of colour, starch intended for the finer technical uses is pure white, but some other products, such as cornflour, may have a decided creamy tint. Differences in methods of manufacture are reflected to some extent in the composition of the product, i.e., in the proportion of non-starchy matters present. As a rule, the moisture-content is between 12 and 15 per cent. Nitrogenous matters, calculated as protein, vary as a rule between 0·2 and 0·5 per cent., but in inferior products they may be as much as 1 per cent. The fat-content varies between 0·02 and 0·1 per cent. The mineral matter in starch purified without alkali is usually 0·1–0·2 per cent., whilst in alkaline starches it is commonly 0·3–0·5. Saare has placed on record the results of determinations of acidity or alkalinity of a number of commercial maize starches, some intended for technical uses and others as foods. In four samples of food starches of British and American manufacture he found alkalinities ranging from 37 to 48 c.c. $N/10$ per 100 grams of dry starch. These were obviously purified by alkaline treatment. Ten samples of German technical and food starches showed acidities up to 25 c.c. $N/10$ per 100 grams.

# CHAPTER IX.

# MANUFACTURE OF RICE STARCH.

RICE (*Oryza sativa*) is cultivated only in tropical or subtropical lands, most extensively in southern and eastern Asia, where it forms the staple foodstuff of vast populations. It is grown also in various countries bordering on the Mediterranean Sea, and in the central parts of the American continent.

The raw material for the manufacture of rice starch consists mainly of damaged and broken grains, large quantities of which are obtained as a by-product in the cleaning and preparation of rice for the market. The operations involved in the preparation of polished rice, as usually sold in European countries, are as follows:—The raw rice or paddy, from the threshers, is sifted and winnowed to remove foreign matters and dirt, and then freed from its hulls or husks. The hulled product is known as "brown rice" although it is not always brown. The next step is the removal of the more or less coloured skin, leaving "white rice" and yielding rice meal or bran as a by-product. The "white rice" is next polished by a beating operation with leather or felt flappers, and finally it is glazed with a trace of talc, kaolin, gypsum, glucose, glycerine, or mineral oil. The composition of rice at these different stages of milling is shown in Table VII, based on data published by Sir John Harrison and C. K. Bancroft.[1]

The broken rice employed for starch manufacture may consist of mixtures derived from all these types of products. Its usual range of composition is as follows:—moisture, 10–14 per cent.; protein, 6–9 per cent.; fat, 0·4–0·8 per cent.; starch, 70–78 per cent.; sugar and gums, 0·8–1·5 per cent.; fibre, 0·3–1 per cent.; ash, 1–2 per cent.

[1] *Journ. Board of Agric. Brit. Guiana*, **1926**, **19**, **32**.

Starch was first manufactured from rice about the middle of the nineteenth century in England. It is now manufactured to some extent in most industrial countries. The world production is much less than that of potato starch or maize starch, but exact data are lacking. Holland, Belgium and Germany export considerable amounts, and there are rice starch factories also in France, Italy, Great Britain and the United States. In 1924, Great Britain exported 17,495 cwts. of rice starch, chiefly to Colonial markets, and imported 106,759 cwts. from Holland, Belgium, Germany, Italy and France.

TABLE VII.

PERCENTAGE COMPOSITION OF RICE PRODUCTS.

| | Paddy. | Brown rice. | White rice and Polished rice. |
|---|---|---|---|
| Moisture .. .. | 12·6 | 11–12 | 12–14 |
| Protein .. .. | 6·1 | 8–8·5 | 7–8 |
| Fat .. .. .. | 2·0 | 2·0 | 0·2–0·5 |
| Starch, sugar, gum .. | 74·1 | 76–78 | 77–79 |
| Fibre .. .. .. | 4·0 | 1 | 0·1–0·5 |
| Ash .. .. .. | 1·2 | 1–1·5 | 0·4–0·6 |

## EXTRACTION AND PURIFICATION OF RICE STARCH.

As a raw material for the manufacture of starch, rice differs from any of the raw materials of the sister industries in its high starch-content, in the extreme smallness of its starch granules, and in the fact that these granules are so tightly packed together and surrounded by insoluble gluten that it has hitherto been found impracticable to effect a satisfactory extraction of the starch without the use of chemical agents. The agent usually employed is caustic soda. It was first proposed for this purpose by Orlando Jones, who operated a starch factory in London, and the process patented by him in 1840 will be described in outline here, as it embodies the general principles of the processes now in use.

The process of Orlando Jones was as follows:—100 parts of rice were steeped in 500 parts of a 0·3 per cent. solution of caustic soda in an iron or copper vessel for 24 hours, and then the liquid was drained off and replaced by twice its bulk of water, which, after a thorough stirring of the contents of the vessel, was also drained off. The steeped rice was then crushed between rollers or ground between mill-stones and sifted on a sieve provided with brushes. The residue remaining on the sieve was again ground and sifted until substantially free from starch. The fine starchy material which passed through the sieve was stirred continuously for 24 hours in ten times its weight of 0·3 per cent. caustic soda solution, and afterwards allowed to stand at rest for about 70 hours. The cloudy supernatant liquor, containing dissolved gluten, was then drawn off as completely as possible and the raw starch stirred up with pure water double the volume of the previous liquor. After standing for an hour to allow heavy impurities to deposit, the starchy liquid was passed through several sieves of fine silk gauze, and left for 70 hours to deposit. A second washing usually sufficed to yield a commercially pure starch.

Modern methods of extracting rice starch are in most cases developments of this process, and the modifications made will be dealt with under the headings of the successive operations.

*Steeping.*—This is commonly carried out in rectangular iron or cement vats about three feet high and with a capacity of about 150 cubic feet. One or two inches above the floor of the vat is a perforated false bottom on which the rice is loaded to a depth of about 16 inches. About 400 gallons of steeping liquor containing 0·3–0·5 per cent. of caustic soda are used per ton of rice. The charge is stirred at intervals of about 6 hours and the steep liquor is drawn off after 18–24 hours and if necessary replaced by fresh. The dissolved protein contained in the liquor drawn off may be precipitated by neutralising with acid and collected for use as fodder. The steeping process is complete when the grain can be crushed between the fingers.

A more modern form of steeping vessel or macerator, which is said to shorten the steeping process very considerably, consists of a tall cylindrical metal tank with a conical bottom having a discharge outlet for the steeped rice, and with pipe connections for circulating the contents of the vessel by injection of air, and for introducing and draining off liquor and washing water.

The object of using caustic soda in the steep is to loosen, and in part dissolve the albuminoid or glutinous matters which hold the starch granules together. Its concentration in the steep liquor must depend upon circumstances. With the concentrations mentioned above there is risk of some of the starch granules becoming swollen or gelatinised, especially in warm weather. The temperature is an important factor, but it must be borne in mind that part of the alkali in the steep liquor is neutralised or rendered inactive by combination with the proteins of the rice and by interaction with the mineral salts of the rice and the steep liquor. Furthermore, the action of micro-organisms in the steep may produce carbonic acid and organic acids, which still further reduce the effective concentration of the alkali. Hanemann recommends 0·2–0·3 per cent. of caustic soda when the starch is subsequently to be separated by sedimentation, and double these concentrations when centrifugal methods of separation are used. In order to hasten the steeping process, and thus reduce the risk of fermentation, which causes inconvenience in the later operations, Berger has proposed concentrations of alkali up to 0·9 per cent., combined with systematic circulation of the steep liquor and artificial cooling in warm weather.

*Milling.*—The steeped rice, which contains about 40 per cent. of moisture, is ground in presence of a further quantity of dilute caustic soda solution of about the same concentration as that employed in the steep. This alkali assists the disintegration of the grain by dissolving and loosening the gluten which holds the starch granules together.

The oldest forms of milling plant for rice are stone mills, and these are used more than any other type to-day. A modern form of stone mill by Uhland consists of two pairs of horizontal stones, viz. an upper pair provided with a hopper and a feed roller, and a lower pair which receives the partially ground material from the upper one and completes the grinding. Two parts of dilute caustic soda solution are supplied to the mills for one part of rice, so that the milled product is a milky fluid containing about 20–28 per cent. of solid matter. A double mill of this type will grind 10 tons of rice in 24 hours.

Roller mills of multiple type are employed in some rice starch factories. A cheaper substitute, the so-called cone mill, is said to give good results with a small consumption of power and without requiring much attention. The cone mill consists of a fluted steel cone rotatably mounted on a horizontal shaft inside a fluted casing of the same shape. The mixture of steeped rice and alkaline liquor is fed from a hopper into the space between the cone and the casing, where the grains are disintegrated by rubbing against one another and against the metallic surfaces. The space between the cone and the casing, which determines the fineness of the product, can be adjusted while the mill is working, by displacement of the rotating cone on its axle.

*Separation of the Starch.*—The thick milky liquid from the mills, containing the finely ground rice in suspension, may be treated in different ways. In some factories the first operation consists in separating the raw starch from the coarser particles and fibrous matters by means of sieves. An alternative procedure is to postpone the use of sieves until a partial separation has been effected by deposition either in vats or in centrifuges. If the material from the mills is diluted with water (say to a solid-content of 2–3 per cent.), stirred thoroughly, and allowed to stand for a time, a large proportion of the coarser impurities will settle out whilst the bulk of the starch remains in suspension, for rice starch subsides very slowly owing to the extremely minute size of its granules. When the coarser matters have deposited, the supernatant starch suspension can be transferred to another vat for sedimentation, or can first be passed through a fine sieve. The impure deposit in the first vat will of course contain a certain amount of starch, which can be recovered by stirring with water, allowing the impurities to subside again and drawing off the upper liquor as before. These operations can be repeated if necessary to recover all the free starch in the residue.

If the milky product from the mills is to be treated centrifugally, it is kept fairly concentrated, so as to contain about 20 per cent. of solids, and spun in a centrifuge with a non-perforated drum, as described more fully on p. 169. In this case the deposit formed consists of three strata, viz. an outer one next to the walls of the drum, consisting of coarse particles together with starch, an intermediate stratum of fairly pure starch, and an inner, softer layer containing glutinous starch and fine fibrous matters. This inner layer is scraped off before the main starch cake is removed from the drum. The cake may then be mixed with water to form a 20 per cent. suspension and passed through a sieve.

These methods of treating the material from the mills, in vats and centrifuges, relieve the sieves of a large amount of work, and avoid the deterioration which silk gauze sieves are apt to suffer by contact with the alkaline mill liquors.

In some factories, however, it is the practice to send the ground product from the mills directly to the sieves. Formerly shaking sieves were the prevailing type in rice starch factories, but it is now more usual to instal revolving cylindrical or hexagonal sieves fitted with very fine wire gauze or with silk gauze. A common form consists of a hexagonal frame about 15–20 feet long, covered with gauze. It is most convenient for the gauze to be fitted in sections on removable insets or panels, which can easily be replaced in case of a puncture or rent. A slight inclination of the revolving sieve ensures the slow travel of the material from one end to the other. A hollow axle shaft with fine perforations supplies water, which washes the starch through the sieve walls. The exhausted residue discharged from the lower end of the sieve consists of fibre and gluten and fine particles of rice which have escaped complete disintegration in the mills. This residue is usually employed as fodder.

The starch suspension which passes through the sieve is treated either in settling vats or in centrifuges, for the separation and purification of the starch. Starch tables are not used for rice starch as this deposits too slowly. When settling vats are employed, the starchy liquid from the sieves is diluted to a specific gravity of about 2°–3° Tw. (sp. gr. 1·01–1·05) and left to stand for about an hour for heavy impurities to subside. The supernatant liquor containing almost all the starch is then transferred to other vats, in which sedimentation is complete in 2–3 days. The surface layers of the starch deposit consist of fine glutinous matter, and any starch cells which have been attacked and rendered light by the alkali. The lower layers, consisting of fairly pure starch, are again stirred up with water and left to deposit.

Centrifuges are very commonly employed in rice starch factories, replacing settling vats either wholly or in part for the purification of the starch. Although much more costly than vats, in power and manipulation, they save a great amount of space and time, and reduce the danger of deterioration of the starch by fermentation. The centrifuges employed for raw rice starch are fitted with drums without perforations. Each charge of starch suspension has to be spun for about 15–20 minutes to separate the starch. After the drum has been brought to rest and the liquor from which the starch has separated has been run out, the layer of impure or glutinous starch is removed from the surface of the pure starch by scraping or brushing. If the original starch suspension was thin, so that the deposited starch layer is also thin, further charges may be spun without removing the pure starch, only the surface layer of impure starch being removed each time.

The succession of operations employed for the purification of the raw starch varies in different factories. Usually there are at least two washings and depositions, either in vats or in centrifuges, besides treatment on fine sieves. In some cases the purified starch is collected finally in filter-presses.

In some factories only one grade of starch is produced, that which cannot be raised to the same standard of quality as the main product being disposed of, together with glutinous waste, as cattle food. In other cases first and second grade starches are produced. The yields of these two products depend on the efficiency of the factory operations and particularly on the milling. It is possible to obtain 75 parts of first-grade starch (containing 15 per cent. of moisture) and 5 parts of second product per 100 parts of rice.

The low-grade by-products from which no marketable starch can be recovered are disposed of as fodders or fertilisers. A considerable proportion, often more than a fifth, of the total protein of the original rice is contained in solution in the alkaline waste waters from the steep and in those separated from the ground rice in the settling vats or centrifuges. The latter liquors carry with them a small quantity of suspended starch, which may be recovered by deposition in large tanks. After the separation of this starch, the liquors are treated to recover the dissolved protein or gluten in them. For this purpose their alkalinity is neutralised by addition of a suitable acid, such as hydrochloric acid, whereby the proteins become insoluble and are precipitated. It is said that satisfactory precipitation has also been brought about by passing carbon dioxide (in the form of flue gases) into the alkaline liquors until the caustic soda present has been converted into sodium bicarbonate. The precipitated protein is collected in filter-presses and dried. It contains about 15 per cent. of nitrogen and is often disposed of as a fertiliser.

*Proposed Extraction of Rice Starch without the aid of Alkali.*—There have been repeated attempts to dispense with the use of caustic soda in the extraction of rice starch. Two processes which have been patented recently may be mentioned here. In one, patented by Reckitt & Sons, Ltd., and C. H. Hardy,[1] the rice is steeped in cold or luke-warm water for a few hours until sufficiently softened to be ground easily. It is then ground very fine in drums of the pebble-mill type or in stone mills or other suitable mills, until at least 98 per cent. will pass through a sieve of 130 × 130 mesh. Sufficient water is added during grinding to yield a pulp containing 38–40 per cent. of solid matter. The pulp is then further diluted and purified. For centrifugal methods it is reduced to a specific gravity of 18–25° Tw. (sp. gr. 1090–1125) and for

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[1] E.P. 147,255; 1919.

sedimentation in vats it is diluted to 1·5–2° Tw. (sp. gr. about 1010). The rice residues obtained by this process contain 30–40 per cent. of proteins (calculated on dry substance), and being free from chemicals they form a valuable material for foddering and other purposes. If it is desired to adapt the purified starch to produce a transparent jelly on mixing with boiling water, a proportion of caustic soda may be added subsequently.

The second process was patented by E. Schlüter,[1] and is as follows:—Rice is ground with an equal quantity of water in a mill adapted for wet grinding, until a fine smooth, viscous mass is obtained. This may be treated in a centrifuge, whereby three fractions are produced:—

(1) A somewhat turbid liquid, which is run off into a depositing tank; it contains rice protein, which is separated by deposition and dried.

(2) A sludge of glutinous starch.

(3) A compact layer of starch next to the walls of the drum. It is stirred in a vat with sufficient water to produce a suspension of 6°–7° Baumé, and left at rest. A yellowish brown deposit of fibrous matter and gluten settles out, after which the pure starch, still in suspension, is run into another tank through a fine silk sieve, and allowed to deposit. The centrifugal treatment may be repeated to remove a further quantity of glutinous starch, and the purified starch thereby obtained is dried.

## DRYING OF RICE STARCH.

Much importance is attached to the operations involved in the drying of rice starch, particularly when the product is to be marketed as "crystal starch." The latter form of starch consists of elongated and somewhat tapering pieces with sharply defined edges, and has generally been regarded as indicating a starch of the first quality.

There are three stages in the drying of starch for the production of lump or crystal starch. The first consists in the

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[1] E.P. 225,101; 1924.

moulding or draining of the wet starch in the form of blocks until its moisture-content is reduced to 40–45 per cent. The second is the "crusting" stage, during which the blocks are partially dried in a warm chamber, and a discoloured crust forms on the outside. The third stage represents the completion of the drying process, after the removal of the discoloured crust. It is during this last stage that the starch blocks become traversed by cracks, which are responsible for the formation of the so-called "crystals."

The drying process as thus carried out is necessarily slow, and at least until the last stage is reached there is a considerable risk of fermentation in the moist starch. Apart from other undesirable effects, this might spoil the blocks by producing bubbles of gas inside them. To guard against this, a certain quantity of caustic soda solution is sometimes added to the starch before draining. Sulphur dioxide has also been recommended for this purpose. If the colour of the starch is to be corrected or brightened by a trace of ultramarine, this is added when the starch is in the form of a thick suspension ready for the draining or moulding process.

Much of the success of the drying process depends on the satisfactory moulding or draining of the wet starch, which should be so carried out as to produce a block of regular shape, free from flaws and bubbles, and of uniform compactness throughout, without any stratification. Draining in centrifuges is not suitable when crystal starch is required, as it does not fulfil the requirements mentioned. One method of operating is by means of draining boxes about 5 feet long and 9 inches broad and high, with a perforated bottom lined with filter cloth. These are filled with a thick, uniform suspension of the starch, just fluid enough to enable it to flow easily, and the water is allowed to drain away without the aid of suction or pressure. As the level of the starch sinks, more of the suspension may be added, so that finally the drained starch completely fills the boxes. From time to time the boxes are jolted to assist the settling of the moist starch into a compact block. In these boxes the moisture-content of the starch is reduced to about 44 per cent. in 24 hours. The starch is cut out in cubical blocks, which are then ready for the "crusting" oven. A great saving of time, with lessened risk of fermentation, is possible by means of more modern moulding boxes, in which draining is carried out with the aid of suction or air pressure or both. There are several types of apparatus for this purpose. Most of them comprise a number of small rectangular metal boxes with perforated bottoms, below which are drainage or suction outlets connected to a common suction pipe. In a large apparatus by Uhland the suction boxes form compartments in a larger unit, over which, when the boxes have been filled, a massive cover can be fixed, and through this cover compressed air is brought to bear on the surface of the draining starch. By such modern types of apparatus the time required for the draining of the starch can be reduced to about half an hour.

For the next stage of drying, the cubical starch blocks, containing 40–45 per cent. of moisture, are placed on porous earthenware tiles in a "crusting" oven, in which the temperature should not exceed 50°–60° C. The evaporation which takes place in this oven draws to the surface of the blocks soluble impurities which remain there as a brownish stain, extending to a depth of about half an inch or more. After 48 hours, the moisture-content of the starch is reduced to 28–30 per cent., and the crusting stage is at an end. The discoloured surface layers of the blocks are scraped off, involving a wastage of about 20–23 per cent. of the starch. The scrapings may be treated by washing and centrifuging, or they may be mixed with starch undergoing purification.

The starch blocks, from which the discoloured crust has been removed, are ready for the final stage of drying. If lump starch is required, they are broken up into lumps and dried in the air. If crystal starch is to be produced, the blocks are wrapped separately in paper and dried slowly in an oven, the temperature of which is raised gradually to between 30° and 50° C. This stage of drying may take a fortnight or longer. Cracks are produced at the surface of the blocks and gradually extend to the centre. If the temperature of the oven is raised too rapidly, these cracks will be very numerous, and the "crystals" will therefore be too small.[1] A slower and uniform rate of drying will produce fewer cracks, which will extend to the middle of the block by fairly straight paths, and yield good "crystals." If the drying is too slow or the temperature variable, the cracks will be very irregular. Hanemann recommends keeping the blocks in the oven for 2–3 days without heating, then raising the temperature slowly, first to 25° C., after 3 days to 28°, and then gradually to 32° - 35° C.

Rice starch which is to be sold in the form of powder can be dried rapidly provided that the temperature is kept sufficiently low to avoid any gelatinisation. By breaking up the moist starch into small fragments at an early stage in the drying process inequalities of colour due to "crusting," which is liable to occur with large lumps, can be avoided.

Commercial rice starch usually contains 12–15 per cent. of moisture. It is produced in the forms of "crystal," lump, and powder, and commands a higher price than wheat-, maize- or potato starch. Its chief application is in laundry work, for which purpose it is often placed on the market in a number of special forms adapted for particular uses, such as blue starch coloured with ultramarine, cream starch containing an orange or yellow dye-stuff, glossy starch, starch gloss, double starch, etc., consisting of starch admixed with such ingredients as borax, stearin and spermaceti. It is highly valued in laundry work on account of its special suitability for "cold starching," the extremely small size of its granules enabling them, in the ungelatinised state, to penetrate into all the interstices of a fabric, so that when afterwards gelatinised by the hot iron and dried, they stiffen the fabric throughout, and not only on the surface.

Rice starch is employed in cosmetics as an ingredient of face powders.

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[1] Hanemann, *Chem. Zeit.*, 1897, **21**, 482.

# CHAPTER X.

# OTHER COMMERCIAL STARCHES.

## CASSAVA STARCH AND TAPIOCA.

TAPIOCA is made from cassava starch, sometimes known as Brazilian arrowroot, which is extracted from the tuberous roots of the manioc or cassava plant. In many tropical lands these roots provide an important foodstuff for native populations, who either consume them as a cooked vegetable, the tropical equivalent of potatoes, or prepare from them a flour (cassava) which is used for making bread or cakes. It is usually unsafe to eat the roots in the raw state, as they contain small quantities of hydrocyanic or prussic acid, which is poisonous, but which disappears completely during cooking or during the extraction and purification of starch from the roots.

Although originally native to Central America, the manioc plant has been successfully cultivated in all tropical parts of the world. The chief centres of cultivation for the industrial production of cassava products are the East Indian Islands, Brazil and Madagascar. There are two main cultivated species or varieties, viz. the bitter variety, *Jatropha Manihot* Linn., known also as *Janipha Manihot* or *Manihot utilissima*, and the sweet variety, *Jatropha dulcis*, known also as *Manihot palmata*, *M. aipi* or *M. dulcis*. The bitter variety is usually more poisonous than the sweet, in the raw state, but its tubers are commonly larger and richer in starch. Carmody[1] found 0·01–0·035 per cent. of prussic acid distributed throughout the tubers of bitter manioc, whilst in the sweet variety he found similar proportions in the cortical layers of the tubers but only

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[1] *Lancet*, 1900, No. 4019, p. 736.

0·004–0·015 per cent. in the interior portions. According to Dunstan, Henry and Auld,[1] the prussic acid is formed by the action of an enzyme on a glucoside, phaseolunatin.

The manioc plant thrives best in light sandy or friable soil. It is propagated from stem cuttings, which are planted at distances of 3–6 feet, in rows 4–6 feet apart. Under favourable conditions the crop may be ready for lifting in 8–10 months, but in some countries 15 months is the customary period, and usually the tubers continue to increase in size up to two years or even longer. The tubers contain 50–70 per cent. of moisture and 20–30 per cent. of starch, but higher proportions of starch have been reported from bitter manioc.

The methods of preparing the various kinds of cassava products from the roots differ to some extent in different countries. Roots which are to be shipped to Europe for the manufacture of starch may be cut into slices or ground to meal and dried in the sun or on special kilns.

In West Africa a cassava meal, employed as a baking flour, is prepared by slicing the tubers in halves, cutting out the fibrous central portion and then drying them in the sun, after which they are ground to powder and sifted to remove coarse fibrous matters.

A wet process which has been widely used, especially in the West Indies, consists in pulping the washed and peeled roots by means of a simple hand or wheel grater, and squeezing the pulp in coarse bags to expel the juice. This juice deposits a certain amount of fairly pure starch (tapioca meal), after separation from which the juice is evaporated to a syrup known as *cassareep* and employed there in the preparation of the well-known "pepper-pot" sauce. The drained pulp from the bags is rubbed through a coarse sieve, which retains lumps and coarse fibre, and then dried for 3–4 hours on a metal plate heated at first very gently and afterwards more strongly. This product constitutes manioc flour, or farine, as it is termed in the West Indies.

There are other processes in use, in which the pulped roots are washed on sieves to extract the starch, and the latter is

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[1] *Proc. Roy. Soc.*, 1906, B, **78**, 152.

purified more or less completely by well-known methods. In some cases these processes are carried out very imperfectly, with primitive appliances, and so much starch remains in the pulp that this is dried and shipped to large factories for further treatment as manioc flour. In other cases the roots are treated in well-equipped factories, where the extraction of the starch is much more complete.

In the main, the operations involved in the extraction and purification of cassava starch in modern factories are similar to those employed in potato starch manufacture. Indeed, a cassava starch factory which has recently been designed for erection in Madagascar has all the equipment of a modern potato starch factory, the only important point of difference being that, owing to the length of the cassava tubers, a slicing machine is interposed between the washer and the first rasping machine.

Java has a number of large factories. An outline of the method of operating is described by J. A. Fowler (*Commercial and Industrial Handbook on Netherlands, East Indies and British Malaya,* U.S. Dept. of Commerce, 1923). The cassava plant takes 11–13 months to mature in the lowlands of Java, and it is found that a better starch is obtained if the plants are left for 2 or 3 months longer. The roots are rasped and the pulp is carried by water through two revolving cylindrical sieves about 5 feet in diameter and 15 feet long, with a slight downward pitch. The first of these is covered with brass wire gauze through which the starch passes, whilst the residue is discharged from the end of the cylinder. The starch is separated into two grades by passing through the second cylinder, which is covered with coarse cotton cloth, and the two fractions thus obtained pass into settling vats as No. 1 and No. 2 flour. The success of this screening process depends on the regulation of the flow of water. The first-grade product deposits in about 4 hours, but the second takes longer. From the settling vat the first-grade product is taken to a stirring vat, where it is washed, and after being deposited again it is taken to the drying room, which is kept at 42° C. When dry, the starch falls through wire trays on which it is placed, and is conveyed to the flour room, where it passes through a silk screen for sacking.

Cassava starch, apart from its use for the preparation of tapioca, is employed industrially in various directions, e.g. for the manufacture of glucose and dextrin. For laundry purposes it is said to be inferior to rice starch but superior to maize or potato starch, giving a smoother surface and a finer gloss. It has been used for the sizing of cotton yarn, but as it has feebler adhesive powers than some of the other starches, it is best mixed with some wheat flour or maize starch for medium and heavy sizing.

Tapioca is a partially gelatinised form of cassava starch. Van Gorkum[1] describes the following method of preparing it in the East Indies. A charge of 5 kilograms of dry cassava starch is placed in a shallow steam-jacketed pan about 2 feet in diameter, and after it has been spread over the surface of the pan, steam at 3–5 kg. pressure (about 40–70 lb. per sq. in.) is admitted to the jacket. The starch begins to adhere to the pan after 3–4 minutes, and it is then loosened with a small spade to prevent scorching and promote drying. The process is ended when the starch has formed into translucent lumps.

A process employed for making pearl tapioca is very similar to the Eastern method of preparing pearl sago. The cassava starch or tapioca meal, slightly moistened, is placed, in small quantities at a time, on a canvas cloth fastened to a cradle-shaped frame, and subjected to a rotatory motion. It gradually forms into small rounded pellets, which while still soft are taken out and dried in the sun. Finally these pellets are heated, during continuous stirring, on a large shallow iron pan the surface of which is greased with a vegetable tallow. A more modern method is to press the slightly moist starch through a coarse sieve to obtain it in a granular form, and then to stir it continuously on shallow steam-heated pans, or to heat it in revolving steam-jacketed cylinders, until the grains have assumed a vitreous appearance.

Pearl tapioca is usually graded according to size as "bullet,"

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[1] *Oost Indische Cultures*, 1913, Vol. III.

"medium" or "seed." Flake tapioca is made by gelatinising a thin layer of moist cassava starch on heated metal surfaces. The usual limits of chemical composition of cassava starch and tapioca are as follows:—moisture, 9–18 per cent.; protein, 0·3–1 per cent.; fat, 0·1–0·4 per cent.; ash, 0·1–0·8 per cent.; the balance, 81–89 per cent., consisting chiefly of starch. Tapioca resembles prepared sago in that, under the microscope, many or most of its starch granules are seen to have been transformed into shapeless masses of gelatinised starch; but the form of the ungelatinised granules is quite different from that of sago starch.

In 1924 the United Kingdom imported 11,000 tons of pearl tapioca, and nearly 4,000 tons of flake tapioca, besides 23,000 tons of other cassava products, classed as flour and powder.

### SAGO.

Sago consists of starch derived from the pith of the stems of certain palm trees native to the East Indies. In a partially purified form it constitutes the chief foodstuff of the natives of many of the East Indian Islands. It was so used in the time of Marco Polo,[1] who visited the Islands in the thirteenth century. Large quantities of sago products, approaching 50,000 tons, are exported from the Straits Settlements to Europe and other parts of the world, where they are employed for manufacturing purposes, e.g. the production of glucose, and for direct consumption in the form of prepared or pearl sago. The latter consists of partially gelatinised sago starch which has been dried in small nodules or pellets. Practically the whole of the world's supply of sago comes from the East Indian Archipelago, the chief exporting centre for which is Singapore. The greater part is produced in the western part of Borneo (Sarawak), the eastern part of Sumatra, and the Riouw Islands lying between.

The chief sago-yielding palms are *Metroxylon sagus*, known also as *M. laeve* or *Sagus laevus*, and *Metroxylon Rumphii* or *Sagus Rumphii*. The former furnishes most of the exported sago, as it grows chiefly in the western part of the Archipelago,

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[1] *Travels of Marco Polo*, Book III, Chapter XVI.

and therefore nearer to Singapore than *M. Rumphii*, the latter being found chiefly in the eastern part, including New Guinea. There are numerous other palms which furnish sago for local consumption, amongst which may be mentioned *Sagus farinifera, Arenga saccharifera, Caryota urens* and various species of *Metroxylon, Borassus* and *Corypha.*

The sago palm requires a moist soil, and forms extensive woods and plantations along the banks of rivers. It reaches maturity in 7–15 years, and forms a stem 1½–3 feet in diameter at the base, and often over 30 feet in height. It blooms only once, and begins to die after the fruit is formed. It is usually felled for the extraction of the sago shortly before the flower bud opens, as the pith is then richest in starch. The felled stems are cut into convenient lengths, usually about 3 feet, the outer woody rind, about 2 inches thick, is slit lengthwise, and the pith is removed and pounded with water. A rough form of sieve consisting of mats made of palm leaf stems serves to separate the milky starch suspension from the fibre of the pith. The former is run into troughs in which the crude sago starch deposits. These operations are carried out at the sago plantation, but for further purification the moist deposit of crude sago is transported to factories, where it is sifted through cloth and subjected to a simple kind of tabling process, similar in principle to the purification on tables or runs practised in European starch factories. The purified product is slightly coloured when moist, but becomes bleached during the drying process, which takes place on mats in the sun. The dried product is known as "sago flour," and from Sarawak about 20,000 tons are shipped annually to Singapore.

A large amount of raw sago produced in various parts of the East Indies is purified at Singapore and converted either into sago flour or pearl sago. For the latter product the same purification processes are employed as for sago flour, but the product is not completely dried. When sufficient moisture has been removed for the material to be crumbled it is broken up and pressed through a coarse screen from which it falls in small crumbs. These are placed on a cloth which is suspended from the corners by a long stick and expanded into a bag-like form by means of small crossed sticks. By a suitable swinging motion of the cloth the starch, if it contains the right amount of moisture, can be rolled into fairly compact pellets, which, after being screened to remove fine particles and lumps, constitutes pearl sago in the unroasted state. Roasting consists in partially gelatinising and drying the granulated sago. It is carried out in shallow metal pans about 2½ feet in diameter, which are heated to a moderate temperature by a carefully regulated fire.

After the surface of one of these pans has been wiped with a cloth saturated with wood oil, some of the granulated sago, prepared as described above, is poured in and stirred with a wooden tool, at first very carefully, but more freely as the pellets harden. After about 3 minutes they are removed from the pan and passed through a screen to separate any which have adhered together. The rest form a steaming heap which is left undisturbed for 12 hours. At this stage the grains have acquired a certain degree of toughness although they are still soft; and most of them are translucent. They are subjected to a second roasting, which renders them hard and tough and greatly reduces their size. This method of making pearl sago was first employed at Singapore about a hundred years ago, but it was known and practised elsewhere before that date. In Europe modern machinery is available for carrying out the process and will be described later in connection with the manufacture of potato sago (see p. 182).

Sago grains swell in cold water owing to the fact that a large number of their constituent starch granules have been gelatinised and therefore consist of dried starch paste. Under the microscope, the swollen sago grains are seen to consist of masses of gelatinised starch together with fragments of partly gelatinised granules and numerous granules which have escaped gelatinisation and therefore preserve their original form.

On the average, genuine sago contains about 12–17 per cent. of moisture, 0·1–1 per cent. of protein, 0·1–0·4 per cent. of fat, 0·1–0·4 per cent. of fibre and 0·1–0·7 per cent. of mineral matter.

The sago products exported from the Straits Settlements (chiefly through Singapore) amount to about 50,000 tons annually. By far the greater part consists of sago flour, and more than half is shipped to the United Kingdom.

## POTATO SAGO.

For many years a product resembling palm sago in appearance has been manufactured in Germany from potato starch. In the year 1910–1911, more than 2000 tons was made. The potato sago closely resembles palm sago in composition and is practically indistinguishable from it by ordinary chemical analysis. The two products may, however, be readily distinguished by microscopic examination of the starch granules, for although in both cases many of the granules are swollen and burst by gelatinisation, there are always a large number which retain their original form.

The method of producing potato sago is in principle similar to the old process of making genuine pearl sago, already described, but modern machines are employed. The purified potato starch is first brought to such a condition of moistness that it can be broken up into pellets which yet do not readily adhere together. The starch is pressed through a metal plate having circular perforations of the necessary size, the plate being jolted so that the starch drops from it in the form of nodules. These are rounded by being rolled inside a rotating drum, into which a small quantity of powdered starch is also introduced to prevent the pellets from sticking together. After this granulating operation, the grains are sorted by means of sieves to separate those which are not of the right size. They are then spread thinly on trays and introduced into a steaming oven, in which hot air saturated with steam is passed. The effect of this is to moisten and gelatinise the outside of the pellets, and when this has proceeded far enough the supply of steam is shut off and the hot air continued, whereby the gelatinised starch on the outside of the pellets is dried to a hard layer. After the contents of the trays have cooled, the pellets, which are stuck together, are broken free from one another, again sorted by means of sieves and finally passed through a polishing machine.

To obtain a yellowish or reddish tint similar to that of some palm sagos, caramel, *caput mortuum* or red oxide of iron is sometimes employed, according to Rehwald.

## ARROWROOT AND OTHER STARCHES.

The name Arrowroot, said to be a corruption of a native American word *araruta*, meaning root flour, is applied in its strictest use only to starch obtained from the rhizomes of the tropical plant *Maranta arundinacea*, or the closely related *M. indica*, *M. nobilis* and *M. ramosissima*. This plant is a native of Central America, but it has been cultivated in many other parts of the world, including the East Indies, Australia and Natal. The West Indies have always been pre-eminent in the production of *Maranta* starch, which is often known as West Indian arrowroot to distinguish it from other products to be described later. In the middle of last century, Bermuda had the reputation of producing the best arrowroot; Jamaica and, later, Natal also exported considerable quantities. The output of these places, at least for export, has now become insignificant, and most of the arrowroot that comes to Europe is produced in the island of St. Vincent, which exports about 20,000–30,000 cwt. annually, chiefly to the United Kingdom.

*Maranta arundinacea*, from which West Indian arrowroot is obtained, is a plant which grows to a height of 2–5 feet and bears large leaves, shaped like arrow-heads. The root subdivides just below the surface of the soil and sends down several rhizomes, about 9–18 ins. in length and as thick as a man's finger. The cultivation of the plant is very similar to that of the potato, but 10–12 months are required for the roots to attain their maximum starch-content, which amounts to about 25–30 per cent. A fairly light soil is most suitable. Absence of rain is not essential, but it is important that there should be no frost during the first 9–10 months, and after that none of sufficient severity to injure the roots in the ground. Given suitable fertilisation of the soil, *Maranta* can be grown in the same ground for many years in succession. The plants are sown in rows from portions of roots or from young off-shoots of stems. Other crops may sometimes be planted between the rows.

According to an account of the production of arrowroot in St. Vincent, by J. W. Macdonald[1], the plants grow to a height of 2–3 feet and are ripe for pulling in 10–12 months. The long roots have joints at intervals of $\frac{3}{4}$–1 inch and are protected by a fibrous covering which grows from each joint, the folds overlapping each other to the end of the root. The fully grown roots are 10–18 inches in length. After they have been cut off, their upper ends, which are relatively poor in starch, are returned to the soil for the propagation of the next crop. The first step in the factory operations is the soaking of the roots in water, to soften the adhering soil and the fibrous covering. The covering is then stripped off and the roots are again washed. The skin is said to contain a resinous substance which gives a yellowish colour and an unpleasant flavour to the starch if the latter is not well washed. The roots were formerly skinned with knives of German silver, and pulped in roller mills, but the former tedious operation has now been discontinued, and the pulping is carried out with rasping machines like those employed for potatoes. The fibrous character of the pulp is apt to cause the latter to collect in lumps if mechanical washing-out apparatus is employed, so it is usual to wash the pulp by hand in a current of water, in a perforated box. The starch suspension which passes through the perforations is conducted through a series of wire-gauze sieves, the first having a mesh of 40, the second 80, and the last 100 to the inch. The starch is deposited in glazed vats, again mixed with water and passed through a fine sieve, and finally deposited in small round galvanised iron cisterns. The deposited starch cake is freed from discoloured surface layers, drained for 12 hours on trays, and then broken into lumps and dried on wire screens in a building open to the air, but protected from birds, etc., by wire netting. The starch crumbles as it dries, and is obtained finally in a

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[1] *J. Soc. Chem. Ind.*, 1887, **6**, 334.

fine granular state containing 14–17 per cent. of moisture. The drying process occupies 3–4 days in hot weather, but in cold wet weather a fortnight may be necessary, and in this case the starch is very liable to become sour and discoloured. The average yield of air-dried arrowroot is about 19 per cent. of the weight of the roots worked, corresponding to about 22 cwt. of arrowroot per acre.

Commercial arrowroot is a fine white product containing 13–17 per cent. of moisture and 81–85 per cent. of anhydrous starch. The amount of protein is usually less than 1 per cent., whilst fat, fibre and mineral matter are present in much smaller amounts. Arrowroot has long enjoyed the reputation of having special nutritive qualities and being particularly suitable for infants and invalids, but it is difficult to say why this should be so. Macdonald refers to it as the most digestible and palatable of the starches, and states that it swells much more readily in hot water than maize-, rice- or wheat starch, and forms a stiffer jelly. It commands a higher retail price than any of the other common starches and is employed chiefly as a foodstuff.

## OTHER STARCHES.

In addition to Maranta starch, or West Indian arrowroot, there are several other so-called arrowroots which are or have been articles of commerce.

East Indian arrowroot, known also as Tik, Tikur, or Travancore starch, is produced in Southern and Eastern Asia and particularly in the neighbourhood of Madras and the Malabar Coast of India. It is derived from two or three species of *Curcuma*, viz. *C. angustifolia*, *C. leucorrhiza* and *C. rubescens*, the roots of which are rich in starch. Some Curcuma starch is white and some is brownish in colour. According to Semler,[1] it does not come into European commerce, unless perhaps as an adulterant of *Maranta* starch, but it is easily distinguished from the latter under the microscope by its flat granules with their very pronounced striae and their

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[1] *Die Tropische Agrikultur*, 1900, Vol. II, p. 749.

one rounded and one abruptly tapering end at which the hilum is situated.

Portland arrowroot is said to be derived from *Arum maculatum*, which according to Wiesner is a native of Southern and Middle Europe, and is cultivated in India. *Arum esculentum*, known also as *Colocasia esculenta*, is grown in the East and West Indies, South America, the South Sea Islands, Japan, the Molucca Islands, Syria and Egypt. Its tubers contain about 20 per cent. of starch. The tubers of *Arum macrorhizum*, or *Alocasia macrorhiza*, also furnish a part of the arrowroot of the South Sea Islands.

Tahiti arrowroot, or Williams' arrowroot, is derived from the tubers of *Tacca oceanica*, or *Tacca pinnatifida*, which grows wild on the sandy shores of the South Sea Islands, where it is known as Pia. It is cultivated also in the Molucca Islands, in India and in Zanzibar and Brazil. The potato-like tubers, which in the wild plants are bitter, have become mild and fleshy by cultivation and contain 28–30 per cent. of starch. According to Wiesner, Brazil and Tahiti produced commercial Tacca starch from early times, but Semler states that it is now made chiefly in the island groups of Raiatea, Huahine, Bora Bora and Maupite. There is a considerable trade amongst the islands, but little of the starch comes to Europe.

Brazilian arrowroot is cassava starch from *Manihot utilissima*.

Dioscorea starch is derived from *Dioscorea alata*, or Yam, which is a perennial climber, native to the East but grown also in Central America. The tubers are as large as coconuts and contain, according to Sir John Harrison and C. K. Bancroft,[1] about 20 per cent. of starch. In 9–11 months the plant yields a crop of 1½–3 tons of tubers per acre. The starch from it is sometimes known as Guiana arrowroot; in Brazil it is called *Farinha de Cara*, Cara being the name of the cultivated plant.

Canna starch, Tous-les-mois starch, or Australian arrowroot is prepared from plants of the genus *Canna*, of which many

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[1] *Journ. Board of Agric. of British Guiana*, 1926, **19**, 20.

species are cultivated for the sake of their tubers. The most important is *Canna edulis*, a native of Peru, where it is known as Adeira, and where its tubers are eaten as Europeans eat potatoes. It has long been cultivated in Eastern Australia, and in Queensland it is said to have replaced *Maranta*, as it gives a better yield of starch although not commanding so high a price. The name *Tous les mois* is said to be a corruption of the native name *Toloman* or *Tulema*. The granules of the starch of *Canna edulis* are larger than those of any other starch, with the exception of that contained in the seeds of the potato.

# CHAPTER XI.

## STARCH PRODUCTS.

### SOLUBLE STARCH.

NUMEROUS processes have been patented for the conversion, on the industrial scale, of starch into a form soluble in hot water[1]; in most of them, starch is treated either with acid or with an oxidising agent The similarity of the products obtained by the two modes of treatment does not appear yet to have found an explanation.

F. Virneisel[2] digests starch with water containing 1–2 per cent. of mineral or organic acid at 50–55° C. until the starch is rendered soluble; the conversion is said to take 15 hours.

C. B. Duryea[3] modifies starch to such a degree that it forms a less viscous paste than ordinary starch with hot water, but not so far as to convert it into soluble starch, by suspending it in warm water with 1 per cent. of acid and keeping the temperature at 55–59° C. until the desired modification is attained. The product is then washed and neutralised with alkali.

L. Blumer[4] heats starch with about 1 per cent. of a volatile organic acid in 10 per cent. aqueous solution. The heating is effected in a jacketed vessel fitted with a stirrer and stillhead, the mixture being kept at 90–100° C. for 2 hours and then at 115° for 4 hours. A fine white product is said to be thus obtained and the acid is recovered and used again.

C. F. Cross and J. Traquair[5] heat dried starch with ⅛–½

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[1] For laboratory methods of preparing soluble starch, see pp. 54–56.

[2] E.P. 12,020 of 1898.

[3] E.P. 11,442 of 1901.

[4] E.P. 10,872 of 1902.

[5] E.P. 9868 of 1902.

its weight of glacial acetic acid in a steam-jacketed vessel for 1–2 hours, the soluble or acetylated starch thus produced being freed from acid and dried.

F. Baeyer & Co.[1] treat starch with a small amount of mineral acid in presence of acetic acid; the starch is thus rendered soluble in hot water, probably owing to its conversion into an acetyl derivative.

Various oxidising agents have been proposed for converting starch into the soluble form; the amount of oxidising agent used is generally small in comparison with the amount of starch transformed.

A. Ashworth[2] proposes to use chlorates in presence of a mineral acid, Soc. Anon. Trust Chimique[3] use a solution of ammonium persulphate, O. Bredt & Co.[4] treat starch with a hot solution of permanganate and F. Fritsche[5] heats starch with a perborate solution. According to E. Flick, the use of per-salts, such as persulphates, for making soluble starch has the disadvantage that much of the active oxygen escapes without taking part in the reaction, and he proposes a method[6] for regulating the liberation of the active oxygen by the addition of certain salts so that its oxidising action is more completely utilised. A suspension of finely divided starch in cold water is treated with a small quantity of aluminium hexachloride, ferric chloride or zinc chloride (preferably the first), and then, whilst the mixture is well stirred, sodium persulphate or other per-salt is added in small portions until the whole of the starch has been rendered soluble. The starch is then washed with cold water, filtered and dried.

Other oxidising agents proposed for rendering starch soluble include chlorine gas,[7] atmospheric air in presence of a dilute acid and suitable catalysts,[8] and hydrogen peroxide.

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[1] F.P. 383,902, 1907.

[2] E.P. 19,720 of 1901.

[3] G.P. 134,301 of 1901.

[4] E.P. 22,370 of 1903.

[5] E.P. 1351 of 1908.

[6] E.P. 25,121 of 1909.

[7] H. Kindscher, G.P. 168,980, 1902; Siemens & Halske A.-G., U.S.P. 798,509, 1905.

[8] A. Paira and Die Administration der Minen von Buchsweiler A.-G., E.P. 9870 of 1909.

C. Sunder[1] obtains transparent pastes containing soluble starch, suitable for finishing fabrics, by heating starch with water containing a small proportion of hydrogen peroxide or sodium peroxide.

The use of pancreas or pancreas extract for converting starch into a soluble form has been proposed by Maison Lepetit, Dollfus & Gannser.[2]

Beside the numerous methods for the manufacture of soluble starch, various processes have been devised for converting starch into products which form adhesive pastes or mucilages with cold water. Most of these processes consist in treating starch with alkaline substances in one form or another. Thus H. Wulkan[3] dries a mixture of starch and ammonia solution in thin layers by hot plates or rollers; the product yields an adhesive paste with cold water. The Arabol Mfg. Co.[4] obtain a product capable of swelling in cold water by treating starch with a thiocyanate. Thus, dry powdered starch (100 parts) is mixed with a 50 per cent. solution of ammonium thiocyanate (80 parts) to which alcohol (40 parts) has been added. The product is freed from thiocyanate by washing with alcohol or acetone; it yields a paste with cold water which appears to possess all the properties of ordinary starch gelatinised at high temperatures.

A. S. Hoyt[5] gelatinises wheat starch by heating with just enough water to prevent burning and then dries and powders the product; it yields an opalescent jelly with water.

F. Sichel Komm.-Ges. and E. Stern[6] mix starch with a little sodium aluminate or silicate and make the mixture into a paste with a quantity of water equal to about 75 per cent. of the weight of starch, the paste being dried at a high temperature. Interaction between the sodium salt and water at the drying temperature produces a small quantity of alkali, but no swelling of the starch occurs such as happens when starch

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[1] *Bull Soc. Ind. Mulhouse*, 1924, **90**, 558.
[2] F.P. 466,275, 1913.
[3] G.P. 223,301, 1908.
[4] F.P. 394,167, 1908.
[5] U.S.P. 1,148,453 and 1,148,454, 1915.
[6] G.P. 389,748, 1920.

that has been treated with alkali in the usual way is dried, although quite as satisfactory modification is obtained and drying is more readily effected.

A. Singer[1] obtains a product capable of swelling with cold water by simultaneously dry-grinding raw starch, and intimately mixing it with dry caustic alkali.

L. Runge[2] obtains a product readily forming a paste with cold water by stirring starch with a saturated solution of an alkaline earth hydroxide at 70–80° C. until the starch ceases to swell, the mass then being filtered, pressed, dried, powdered and mixed with sufficient finely divided oxalic acid to neutralise any residual alkali.

J. Kantorowicz[3] obtains an adhesive from potato starch by treatment with a peroxide or per-salt having an alkaline reaction, or with a neutral peroxide or per-salt in an alkaline medium, the proportions being such that complete transformation of the starch into soluble starch is avoided.

## DEXTRIN.

In the purely scientific sense the term "dextrin" comprises the degradation products of starch of the general formula $(C_6H_{10}O_5)n$, which are soluble in hot and cold water, insoluble in alcohol and ether, dextrorotatory, non- or only slightly copper-reducing, almost unfermentable, and give either a red colour (erythrodextrin) or no colour with iodine. The nature of these substances and their relation on the one hand to starch and on the other to sugar is considered in Chapter III.

In the industrial sense, the term "dextrin" is applied more loosely to denote the various products obtained by roasting starch either alone or with a small quantity of acid. These products are more or less soluble in cold water and almost completely soluble in hot water, and in addition to dextrins they contain more or less soluble starch and sugar; some commercial dextrins approximate in composition to soluble starch, whilst others at the other end of the scale, approach starch sugar or starch syrup. C. Scheibler and H. Mittelmeier[4]

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[1] E.P. 188,344, 1922.

[2] G.P. 381,516, 1922.

[3] E.P. 179,765, 1922.

[4] *Ber.*, 1890, **23**, 3060.

found that commercial dextrin contains appreciable quantities of dextrose and that it can be purified by repeated precipitation with alcohol or by osmosis; the purified dextrin thus obtained no doubt consists of a mixture of dextrins. The sugar-content of commercial dextrin does not increase progressively with the duration of the roasting process since part of the sugar (dextrose and maltose) formed initially undergoes reversion to dextrins in the later stages of heating. P. Petit[1] showed that in the dextrinisation of starch by heating with a small quantity of nitric acid the reducing sugar-content of the product is diminished by prolonging the period of heating, or by heating at higher temperatures, observations which account for the fact that some commercial dextrins of a high degree of dextrinisation are practically free from reducing sugar. Wohl,[2] too, showed that commercial dextrin consists in part of dextrins formed by reversion. Whether the dextrins formed by reversion are identical with those formed directly in the roasting of starch is not yet known, nor is it known to what degree the properties of commercial dextrin are due on the one hand to decomposition products of starch, and, on the other, to reversion products of sugars.

G. W. Rolfe[3] has given figures (see Table VIII) for the specific rotatory power and reducing power of a number of samples of commercial dextrin. The concentrations of the solutions used were determined by the solution density method with the factor 3·86 as divisor and the reducing powers are given in terms of that of dextrose as unity.

Rolfe[4] considers, from his investigations, that when starch is heated with a small quantity of dilute nitric acid, as in the preparation of dextrin, a normal hydrolysis of the starch to reducing sugar occurs initially, but very soon ceases owing to evaporation of the hydrolytic agent, although the breakdown of the starch complex continues with the further heating. Rolfe also considers that a reducing power equivalent to more than 2 per cent. of dextrose indicates that the dextrin has been made by an acid process, the amount of acid used being

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[1] *Compt. rend.*, 1892, **114**, 76.

[2] *Ber.*, 1890, **23**, 2104.

[3] *Eighth Int. Congr. Appl. Chem.*, 1912.

[4] *Loc. cit.*

indicated by the excess of reducing power over 2 per cent.; the period and degree of heating are roughly indicated by the specific rotation, which decreases with time and increasing temperature.

Potato starch is the principal raw material used in the manufacture of dextrin, but wheat-, maize-, rice- and cassava starches are also employed. The product is marketed in the form of (1) a powder which exhibits the unchanged structure of the starch granule, (2) amorphous grains resembling gum arabic in appearance, (3) a thick, milky fluid. By far the greater part of commercial dextrin is manufactured in the form of powder and most of the processes described below refer to the production of dextrin in that condition. Powder dextrin is obtained by roasting starch either directly or after treatment with a small quantity of acid.

TABLE VIII.

| Kind of Dextrin. | Iodine Test. | $[\alpha]_D$. | Reducing power. |
|---|---|---|---|
| German Std. Canary | Red | 161·2 | 0·0886 |
| Superior Dextrin | Violet | 174·0 | 0·0342 |
| German Std. White Potato | Wine-red | 176·6 | 0·0778 |
| ,, ,, Light Canary | Red-brown | 156·5 | 0·0673 |
| White Potato | Wine-red | 181·8 | 0·0832 |
| German Dextrin | Red | 169·4 | 0·1508 |
| Potato Canary | — | 156·6 | 0·0778 |
| Tapioca Envelope, No. 1 | Brown | 174·0 | 0·0374 |
| ,, ,, No. 2 | — | 166·2 | 0·0056 |
| Corn Dextrin | Brown | 149·8 | 0·0802 |
| German Std. White Potato | — | 177·1 | 0·0842 |
| Imported English Envelope | Brown red | 180·6 | 0·0420 |
| Imported German Potato Canary | — | 154·3 | 0·0733 |

*Direct Roasting.*—The starch is heated in pans, provided with a stirring device, to 150–250° C. for 2 hours or more until the requisite degrees of colour and solubility are attained, the mass then being cooled, ground and sifted. V. G. Bloede[1] has claimed a process for making adhesive substances from starch, according to which raw starch is heated to 150–200° C.

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[1] U.S.P. 1,324,332, 1918.

for ½–1 hour according to the purpose for which the product is required, the temperature and duration of heating being so regulated that the product remains practically insoluble in cold water.

*Roasting with Acid.*—By carrying out the roasting process in presence of a small quantity of acid the dextrinisation can be effected more rapidly and at a lower temperature than when no acid is used, and the product is, in general, of a lighter colour. The starch may be mixed with the requisite quantity of acid (usually 0·2–0·25 per cent. of hydrochloric or nitric acid) by injecting the latter, diluted with water, into a drum in which the starch is kept well agitated. Any lumps formed in this operation are broken up and the mass is then kept for about 24 hours to insure the thorough admixture of the starch and acid. The mixture is next carefully dried, in order to minimise the formation of sugar in the subsequent roasting operation, ground, sifted and fed to the roasting apparatus, in which it is heated for 1–1½ hours or 2 hours at 100–125° C., according as a white or yellow-coloured product is required. The preliminary operation of incorporating the starch and acid may be greatly shortened or even combined with the roasting operation. Thus H. Wulkan[1] has devised a continuous process, according to which about 5–6 per cent. of the starch is intimately mixed with the quantity of acid (0·2–0·4 per cent.) requisite for dextrinising the whole of the starch, the acid being used in as concentrated a state as possible so that the practically dry powder thus obtained can easily be thoroughly incorporated with the remainder of the starch. The mixture is fed continuously from a mixing vessel through a pair of rollers, to break up lumps, into a steam-jacketed vessel containing dextrin which is kept in motion by a stirring apparatus. The added starch becomes dextrinised almost immediately and the finished product, which has lost practically no moisture during the dextrinising process, is withdrawn through a door at the bottom of the heating vessel.

According to a process of the Dextrin-Automat Ges.,[2]

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[1] E.P. 7032 of 1910.

[2] G.P. 286,362, 1912.

starch is swollen by heating and then mixed with powdered starch which has been treated with concentrated acid. The mixture so prepared is heated slowly in a steam-jacketed vessel to 105–150° C. By varying the rate of heating and the temperature, dextrins of various kinds may be obtained.

Various processes and apparatus have been devised for acidifying the starch just prior to its admission to the dextrinising vessel or after it has actually entered the latter.[1]

Regulation of the temperature at which the acidified starch is heated demands great care, and various modes of heating the dextrinising vessel have been proposed. Uhland's apparatus comprises an inner cast-iron vessel to contain the charge and an outer vessel which is directly heated, the space between being filled with oil. The inner vessel has an outlet for volatile products and is provided with a stirring device, which, turned in one direction stirs the charge and turned in the other empties the inner vessel. In Lehmann's apparatus the dextrinising vessel is air-jacketed, the air space below it containing a number of closed iron tubes partly filled with water. The ends of the tubes extend into a fire and the pressure within them, as shown by a manometer, is kept at about 150 atmospheres. C. Hervey[2] proposes to use vessels so shaped as to insure even heating of the charge; these vessels, 3 ft. 10 in. deep, 4 ft. 6 in. long and 6½ in. wide, are heated in boiling water.

The progress and completion of dextrinisation may be controlled by determinations of the solubility of the product in cold water; a determination can be made in 10–15 minutes (see p. 230). The readiness with which the product dissolves in cold water and the rate of filtration of the solution and its clarity or opalescence should also be noted, since dextrins of equal solubilities may yet differ in these respects.

If the object is to obtain a white dextrin, the product should be cooled as quickly as possible when dextrinisation has been carried far enough. Uhland's apparatus for this purpose

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[1] F.P. 336,903, 1903; E.P. 16,362 of 1914; U.S.P. 1,159,591 and 1,159,592, 1915.

[2] E.P. 16,284 of 1911.

comprises a series of air-cooled, superimposed, shallow, cylindrical wrought iron pans, and a central shaft which passes through all the pans and carries stirring arms in each; the dextrin passes over each pan in succession.

The roasted product contains about 3 per cent. of water, which is increased to the water-content customary in commercial dextrin (10–12 per cent.) by exposing the product in thin layers in a chamber into which steam is injected, or it may be exposed, with stirring, to moist air. According to a process patented by Uhland[1] the dry dextrin descends through a vertical tower, the sides of which are fitted with inclined plates to impart a zig-zag direction to the falling dextrin and a current of moist air is introduced at the bottom of the tower. The dextrin is finally sifted and mixed.

Dextrin, as ordinarily manufactured, has a rather unpleasant flavour and odour and several methods have been proposed to eliminate these objectionable features. According to one process,[2] starch is stirred with a dilute (1 per cent.) solution of acid and left to stand for 24 hours. The deposited starch is then washed with water until free from acid, suspended in water and boiled with 0·5 per cent. of a saturated solution of sulphurous acid under 3–4 atmospheres pressure until the first trace of reducing sugar is formed. The trace of sulphuric acid formed is then neutralised and the solution filtered through animal charcoal and evaporated to dryness. The product has a fine, white colour and is free from the objectionable flavour and odour of ordinary dextrin. In Pieper's process,[3] the starch, after being treated with acid and dried in the usual way, is transferred to the roasting vessel through which a current of ozonised air is passed whilst the starch is being heated; the dextrin thus obtained is said to have a better appearance than ordinary dextrin, and to possess, in solution, a pleasant odour and flavour.

The odour of ordinary commercial dextrin is ascribed by H. Kunz-Krause[4] to the presence of a solid, non-volatile

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[1] F.P. 363,623, 1906.

[2] A. Schumann, E.P. 5460 of 1887.

[3] E.P. 9675 of 1894.

[4] *Ber. Deut. pharm. Ges.*, 1923, **33**, 149.

substance—dextrinozol—which appears to be a cyclic ester of myristic acid; the compound may be isolated by steam-distilling dextrin and extracting the distillate with petroleum spirit.

Granulated dextrin, or "Crystal Gum" as it is sometimes called, is generally prepared by dissolving dextrin powder in hot water, filtering the solution through bone charcoal, evaporating the filtrate to dryness and breaking up or grinding the residue.

Liquid dextrins are obtained by heating starch with such a quantity of acidified water that the product consists of a paste or viscid solution. According to one process[1] a mixture of 5 parts of starch and 8 parts of water containing acid or digesting agent is digested at a temperature below or near the gelatinising point of the starch until the gelatinous character of the starch has almost disappeared; the temperature is then raised above the gelatinising temperature, and the mixture is finally neutralised. The paste thus obtained has a pulpy or unctuous consistency and possesses great adhesive power. According to W. McLaurin's[2] process, a mixture of equal parts of starch and water and a quantity of acid less than 1 per cent. of the weight of the starch is subjected to a temperature of about 138° C. in a steam-heated closed vessel until the starch is converted into dextrin in the form of a colourless solution of about 50 per cent. concentration. The product is suitable as a coating, adhesive or impregnating material for paper, textiles, etc.

*Composition of Commercial Dextrins.*—Commercial dextrins contain 8–12 per cent. of moisture, 3–10 per cent. of reducing sugar (dextrose and maltose) and 0·5 per cent. of ash, and possess an acidity equivalent to 3 c.c. of $N/1$ sodium hydroxide per 100 grms. White dextrins contain 20–75 per cent. of matter soluble in cold water, whilst slightly coloured products contain about 97 per cent., and more highly coloured dextrins are practically completely soluble.

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[1] C. M. Higgins, E.P. 1885 of 1900.

[2] U.S.P. 1,283,839, 1915 and 1,284,120, 1916.

## STARCH SUGAR.

The discovery by G. S. K. Kirchoff,[1] in 1811, that starch is converted into sugar when heated with dilute sulphuric acid formed the foundation of the important industry of the manufacture of starch sugar now so largely used for confectionery purposes and in fermentation processes.

Kirchoff was led to his discovery in an endeavour to prepare a substitute for gum arabic from starch. B. Lagrande, in 1804, had obtained a gum-like substance (dextrin) by heating starch, and Kirchoff attempted to obtain a similar substance by treating a suspension of starch with sulphuric acid, and found that on neutralising the solution with chalk, filtering from calcium sulphate and evaporating the filtrate, he obtained, not a gum, but a sweet syrup which, in the course of a few days, solidified. The method adopted by Kirchoff for the preparation of starch sugar merits description on account of its historical interest. A mixture of 1 part of sulphuric acid and 200 parts of water was heated to boiling, a milk of 100 parts of starch and 200 parts of water then being gradually added. The boiling, carried out in an open vessel, was continued for 36 hours, after which the acid liquor was treated with 10 parts of charcoal and allowed to stand for a few hours, then neutralised with chalk and filtered through flannel. The filtrate was evaporated in shallow vessels to a syrupy consistency and left to crystallise, the solid sugar being placed in filter bags and pressed to free it from mother liquor. The product thus obtained possessed a slight, sweetish odour; it was less sweet in taste than cane sugar, but cleaner in flavour than beet sugar of that date.

The mechanism of the conversion of starch into sugar was first correctly explained as a process of hydration (or hydrolysis) by de Saussure,[2] who also accurately determined the amount of sugar obtainable from a given quantity of starch and showed that the sugar is identical with grape sugar.

The first factory for the manufacture of starch sugar was established in 1812 at Tiefurt by the Grand Duke of Saxe-Weimar and placed under the superintendence of Döbereiner.

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[1] *Schweigg. J.*, 1812, **4**, 108.

[2] *Bull. Pharm.*, 1814, **6**, 499.

This venture was not a success, however, partly owing to the raising of the Continental blockade, which caused a great reduction in the price of cane sugar, and partly owing perhaps to the inferior quality of the sugar produced, and the new industry remained at a standstill for some years.

Kirchoff's original process became much modified and improved by later investigators. Hermstädt shortened the boiling period from 36 to 10 hours by using a larger proportion of acid, and Lampadius substituted steam heating for boiling over an open fire. The subsequent introduction of heating under pressure rendered practicable a much more complete saccharification of the starch with a smaller proportion of acid and in a much shorter time. After its initial check and as a result of the great improvements in the manufacturing process, the potato starch sugar industry rapidly developed in Germany. The manufacture of maize starch sugar was established later in the United States and has there become a very large industry, its recent development being remarkable, the production, which in 1914 was 174,368,818 lbs., amounting to 527,909,513 lbs. in 1923.

Starch sugar is largely used for confectionery purposes, in the manufacture of jam, marmalade and artificial honey, and in fermentation processes; it also finds important applications in the textile, colour printing, paper and leather industries.

Starch sugar is produced in various forms and degrees of purity which may be grouped in the following classes:—

(1) *Starch Syrup, Liquid Glucose or Corn Syrup.*—Starch syrup, obtained by the incomplete hydrolysis of starch or grain is a thick, viscous, uncrystallisable liquid containing from 12 to 20 per cent. of water. It also contains, in addition to dextrose and some maltose, considerable proportions of dextrin and unfermentable carbohydrates (the latter probably formed by the action of the acid on the sugars produced in the first instance), and it is the presence of these substances that prevents the crystallisation of the sugar.

(2) *Solid Glucose.*—Solid glucose, known in the United States as "70 sugar" or "80 sugar" according to the percentage of dextrose it contains, is a micro-crystalline solid, though to

the unaided eye it appears as an amorphous mass of soap-like or harder consistency; its colour may range from almost pure white to dark brown according to the nature of the raw material, method of hydrolysis and degree of clarification.

(3) *Commercial Dextrose.*—Commercial dextrose is a fine crystalline powder containing from 80 to 99·5 per cent. or even more of the pure sugar.

The amylaceous material used for manufacturing starch sugar may consist of the starch from cereals such as maize, wheat or rice, or from potatoes, or it may consist of the cereals themselves, though in the latter case of course the product is liable to be of lower quality.

In the United States, maize starch is used almost exclusively, potato starch being only employed on a small scale. According to E. Parow,[1] analysis shows very little difference between the starch syrups from maize and potato starches, but potato starch syrups usually give better results with the "confectioner's test" (i.e. degree of discoloration when heated to 145° C.); the degree of discoloration is affected by the fat- and protein-contents of the syrups; a syrup containing 0·06 of fat and 0·09 per cent. of protein showed little alteration on heating to 145° C., but other samples containing 0·14–0·19 per cent. fat and 0·19–0·39 of protein were badly discoloured. Parow points out that an excessive proportion of fat in the product may, in many cases, be avoided by limiting the amount of oil added to prevent frothing in the vacuum pan during the manufacture of starch sugar.

The process of manufacture comprises the following operations: (1) hydrolysis, (2) neutralisation, (3) filtration, (4) decolorisation, (5) concentration and (6) crystallisation, and these operations will now be considered in turn.

*Hydrolysis.*—In former times sulphuric acid was the agent most commonly employed for the conversion of starch into sugar, but hydrochloric acid is now very frequently used and, in the United States, it is used almost exclusively. The amount of acid required varies according to the conditions under which conversion is effected; if as is usual in Continental

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[1] *Zeitsch. Spiritusind.*, 1922, **45**, 229.

factories the conversion is carried out under moderate pressure (about 1 atmosphere), the proportions of the reacting substances are of the order of 2 to 4 parts of acid and 150 to 250 parts of water per 100 parts of starch. With such proportions, the temperature at which conversion is effected should not exceed 130° C., and careful superintendence of the operation is necessary to ascertain when saccharification has reached the maximum, since any heating beyond this point causes loss by decomposition of sugar; if the operation is properly conducted a conversion liquor of 92–97 per cent. purity can be obtained. E. Parow[1] investigated the rate of hydrolysis of potato starch by dilute sulphuric acid. The proportions of material used were such that syrups containing 30–35 per cent. of extract were obtained, and four sets of conditions were employed, viz.:—

(1) Boiling under a pressure of 14·5 lbs. with 0·8 per cent. of sulphuric acid (on raw material).

(2) Boiling under a pressure of 22 lbs., acid strength as before.

(3) Boiling under a pressure of 29 lbs., acid strength as before.

(4) Boiling under a pressure of 14·5 lbs. with 1·0 per cent. of sulphuric acid.

Samples of the conversion products were withdrawn at intervals, and the proportions of dextrose estimated.

TABLE IX.

| Period of Heating. | Percentage of Dextrose in Extract. | | | |
|---|---|---|---|---|
| | (1) | (2) | (3) | (4) |
| After 10 minutes under full pressure | 16·02 | 27·17 | 50·2 | 28·9 |
| ,, 20 ,, ,, ,, ,, | 31·06 | 45·5 | 62·5 | 47·2 |
| ,, 30 ,, ,, ,, ,, | 42·5 | 57·7 | 75·16 | 64·2 |
| ,, 40 ,, ,, ,, ,, | 54·3 | — | — | — |
| ,, 60 ,, ,, ,, ,, | 68·7 | — | — | — |
| ,, 80 ,, ,, ,, ,, | 83·3 | — | — | — |

These results show that the rate of hydrolysis increases very rapidly with increasing pressure, but Parow points out

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[1] *Zeitsch. Spiritusind.*, 1905, **28**, 121.

that in the manufacture of starch sugar from potatoes it is preferable to boil under moderate pressure for a longer time in order to expel the odour characteristic of potato starch.

In the United States, a much smaller proportion of acid is generally used in the conversion process than is customary in European practice, but the conversion is usually carried out under a higher pressure. The manufacture of starch sugar from maize starch is generally done in conjunction with the manufacture of the starch itself. Green maize starch (i.e. the moist starch direct from the starch tables) is suspended in water, treated with hydrochloric acid and heated under pressure in large copper converters. The concentration of starch and acid and the temperature and period of boiling are varied according to the nature of the product required. For the production of starch syrup, the suspension or milk of starch should have a concentration of 22° Beaumé, the hydrochloric acid should amount to 0·12 per cent. of the air-dry starch and the conversion should be effected at about 137° C. (a pressure of 2·3 atmospheres) in 5–7 minutes, by which time a sample of the cooled juice should give a red colour with iodine. If the solid, more highly converted starch sugar is required, thinner starch suspensions—down to 10° Beaumé—and larger proportions of acid—up to 0·20 per cent.—are used and the conversion is made at higher temperatures and pressures; the heating is continued until a sample of the juice no longer gives a precipitate of dextrin on treatment with strong alcohol, about 15–20 minutes being required for this, and the heating should be continued for 10 minutes longer if the highest grade of sugar is required.

According to a process described by C. B. Duryea,[1] starch is hydrolysed to dextrose in two stages. In the first stage the starch is suspended in dilute acid, then washed to free it from impurities and finally dried whilst some of the acid is still present. A highly modified, thin-boiling starch is thus obtained which, in the second stage of the process, is diluted to a density of about 16° Beaumé and heated with about 0·05 per cent. of hydrochloric acid for 30 minutes under a steam pressure of 30 lbs. The solution thus obtained is filtered

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[1] E.P. 11,800 and 11,801 of 1907.

and refined by a process,[1] in which the dilute syrup is treated with tannin (1 part to 4800), heated to 90° C., filtered, treated with animal charcoal (1 part to 50 of syrup of 42° Beaumé), filtered again and finally concentrated.

In the manufacture of glucose by the acid hydrolysis of maize starch, an insoluble product, known as "refinery mud," occurs in the solution after hydrolysis is finished, and is separated by filtration. This mud contains about 50 per cent. of fatty matter which, according to T. C. Taylor and L. Lehrmann,[2] consists of palmitic, oleic and linolic acids derived from the starch, with the amylopectin constituent of which these acids appear to be organically combined.

The use of other acids instead of sulphuric or hydrochloric acid as hydrolysts has not found much favour, though various acids have been proposed, e.g. nitric,[3] phosphoric[4] and hydrofluoric acids[5]; the two latter acids have the advantage that they yield insoluble salts with chalk.

The use of mould fungi of various kinds as hydrolytic agents in the manufacture of starch sugar has formed the subject of numerous patents, some of which will now be considered

According to a process described by L. C. A. Calmette,[6] a mash of 1 part of crushed maize or decorticated rice and 2 parts of water is heated with a small quantity of hydrochloric acid (0·5 per cent. of the weight of grain) in three stages of 1 hour each at 100, 110° and 120° C.; the acid is best added in small portions during the boiling process. The product, consisting of a solution of dextrose, maltose and dextrin, is concentrated to about 25 kilos. of grain per hectolitre and transferred to a special saccharifying vessel which is provided with means for aerating, emulsifying and circulating the liquor with sterilised, compressed air. The liquor is then treated with sodium carbonate in quantity sufficient to reduce its

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[1] F.P. 380,680, 1907.

[2] *J. Amer. Chem. Soc.*, 1926, **48**, 1739.

[3] A. Seyberlich and A. Trampedach, E.P. 8000 of 1885.

[4] H. J. Haddon, E.P. 6176 of 1882.

[5] F. Malinsky, *Zeitsch. Spiritusind.*, 1899, **22**, 240.

[6] E.P. 11,622 of 1900.

acidity to a degree equal to 0·25 per cent. of sulphuric acid and inoculated with a vigorous culture of saccharifying *mucedinae* in the form of young mycelia without sporules. The liquor is kept aerated and in the course of 36 hours (or 24 hours if the liquor is pitched with a previously prepared culture) the conversion to dextrose is complete.

B, Hoff, G. H. Zschiesche and K. P. Schürer[1] propose to use *Oidium lactis* as a starch-converting agent; this organism, in presence of the smallest quantity of a saccharifying enzyme such as malt diastase is said to convert starch rapidly and completely into dextrose, no appreciable quantity of maltose or dextrin being formed. To prepare a suitable culture of the organism, potato pulp is boiled with a small quantity of water and the stiff paste thus obtained is cooled to 30° C. and inoculated with a pure culture, the inoculated mass being carefully mixed and exposed in a thin layer at 30–35° C. for 12–18 hours. The preparation thus obtained, when mixed with malt or malt diastase, is suitable for the saccharification of potato pulp or other starchy material.

The Société d'Exploitation des Procédes H. Boulard[2] patented a process, according to which the saccharification of starch is effected by a mould known as *Mucor Boulard No. 5*, which occurs in large quantities on plants in the Far East. The mycelial threads of this organism are septate and terminate in pear-shaped enlargements which become detached in old cultures. In order to obtain products containing much dextrose and very little maltose or dextrin, the amylaceous material (potato- or cereal starch) is heated with water and 0·5–0·8 per cent. of acid under a pressure of 3·5 kilos. for 35 minutes, and then transferred to a closed vat provided with apparatus for aeration and inoculated at 40° C. with a small quantity of the mould. When the conversion is complete the liquid is filtered and it can then be concentrated, no neutralisation being necessary, and colourless syrups may thus be obtained without the aid of charcoal.

*Neutralisation.*—The liquor resulting from hydrolysis of the starch requires to be neutralised if acid has been used as

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[1] G.P. 197,468, 1906.

[2] F.P. 464,601, 1913 and F.P. 477,927, 1914.

converting agent, and this is effected with either chalk or sodium carbonate. If sulphuric acid has been used to effect conversion and subsequently neutralised with chalk, much of the resulting calcium sulphate is eliminated as a precipitate, but if hydrochloric acid has been employed the use of chalk for neutralisation is attended with the disadvantage that the calcium chloride formed remains in the syrup, and, according to E. Preuss,[1] glucose syrups so prepared are not suitable for confectionery purposes, since the calcium chloride that they contain would invert the sucrose in the process of boiling the confectionery. Syrups which have been prepared with hydrochloric acid and are intended for use in the manufacture of confectionery should be neutralised with sodium carbonate, the sodium chloride formed thereby having no hydrolytic action on sucrose; further, if neutralisation is properly carried out, any calcium chloride which may have been formed by the action of the acid on the mineral matter in the starch is removed. W. Ekhard[2] has pointed out that the acidity of manufactured starch syrup may be due to free mineral acid or to acid salts, viz. primary and secondary phosphates; although starch syrup intended for confectionery purposes should have as little free mineral acidity as possible it should not be completely neutral, since otherwise it is liable to develop a yellow colour in the course of confectionery manufacture, and the acidity due to acid phosphates should not be less than 0·3 per cent.

P. P. Budnikoff and A. I. Sworykin[3] have proposed to remove the hydrochloric acid from converted starch syrup by electrolysis; by using a platinum anode in a porous pot containing dilute hydrochloric acid and a platinum cathode in a glucose-hydrochloric acid solution, 98·7 per cent. of the acid can be removed, no decomposition of glucose occurring.

*Filtration.*—After neutralisation, the starch sugar solution is filtered; this is effected with filter presses, one type of which is illustrated in Fig. 50. If sulphuric acid has been used for conversion and chalk for neutralisation the solution will

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[1] *Zeitsch. Spiritusind.*, 1904, **27**, 478.

[2] *Ibid.*, 1923, **46**, 228.

[3] *Zeitsch. angew, Chem.*, 1922, **35**, 677.

require to be filtered again after concentration to thick juice in order to remove a further quantity of calcium sulphate which separates from the latter.

*Decolorisation.*—Decolorisation of the starch sugar solution is effected by passage through bone char filters.

*Concentration.*—The decolorised solution is next concentrated in vacuum pans to a degree depending on the nature of the product desired. If starch syrup or solid glucose is the object of manufacture, the concentration may be continued until the solution has attained a density of 1·5. If, however, crystallised commercial dextrose is required, the solution is only evaporated to a density of 1·36–1·38.

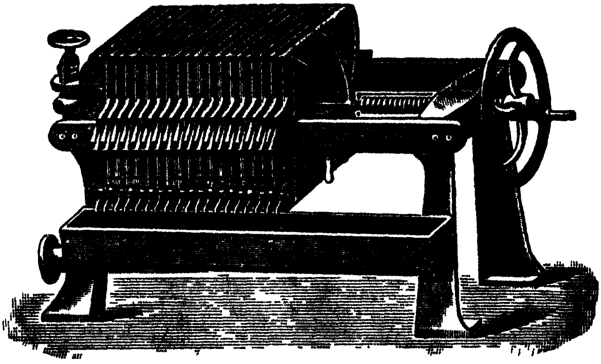

FIG. 50.
Filter press by Uhland.

*Crystallisation.*—In preparing the micro-crystalline solid glucose, the concentrated syrup is merely run into moulds, where, after being seeded with solid glucose and cooled, it soon forms a solid mass, which is broken into lumps and marketed in that form.

To obtain the comparatively pure, commercial dextrose, however, the greatest care must be paid to the crystallisation process. The syrup or massecuite of density 1·36–1·38 is cooled to, and maintained at 30–40° C. At lower temperatures crystallisation is more rapid, but the crystals are so small and ill-defined that they cannot be properly washed; whilst at higher temperatures, although the crystals are large and well-defined,. they are somewhat coloured and the yield of first-product sugar is small. The sugar may be obtained either anhydrous or as monohydrate by seeding the solution with well-formed crystals of either modification; the anhydrous crystallises more rapidly than the hydrated form.

According to W. B. Newkirk,[1] commercial dextrose of high quality is obtained by carrying the acid hydrolysis of starch as far as possible, filtering the converted liquor through a bone char filter, concentrating and crystallising at about 38° C. in a jacketed crystallising vessel provided with a stirrer. The sugar is separated in a hydro-extractor and washed with water; it should have a purity of 99–100 per cent. The mother liquor is further worked up and, if a high-grade starch has been used, a second crop of dextrose of high purity may be obtained.

According to H. Berlin,[2] the final mother liquor in the manufacture of glucose from maize starch contains gentiobiose. The solid matter in this mother liquor comprises about 70 per cent. of fermentable and 30 per cent. of unfermentable matter, the former being chiefly glucose. From the unfermentable part, Berlin has isolated 18·3 per cent. of gentiobiose. No doubt the sugar is a reversion product from glucose.

Although the manufacture of starch sugar has been an important industry for many years, the preparation of refined dextrose on a large commercial scale is a comparatively recent development. According to L. K. Arnold,[3] pure dextrose is made on a large scale by several firms in America. Thus, Corn Products Refining Company has recently built a factory at Argo, Illinois, which is said to be capable of turning out 600,000 lbs. per day.

The preparation of dextrose of high purity for laboratory purposes is conveniently effected by boiling the commercially pure sugar with methyl alcohol of about 90 per cent. concentration; the hot saturated solution is filtered (the commercial sugar prepared from starch is likely to contain a trace of dextrin which remains undissolved in the alcohol), and the filtrate left to cool and stand for some days; the $\alpha$-isomeride

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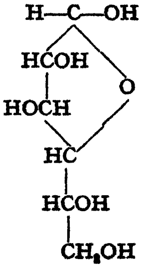
[1] U.S.P. 1,471,347, 1923.

[2] *J. Amer. Chem. Soc.*, 1926, **48**, 2627.

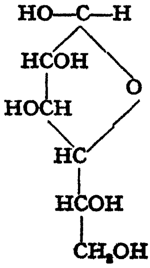
[3] *Facts About Sugar*, 1926, **21**, 638.

(see below) is thus obtained. Acetic acid is another useful solvent for purifying dextrose and it has been shown by C. S. Hudson and J. K. Dale[1] that according to the conditions under which this solvent is used either α- or β-dextrose (*ibid.*) may be obtained. Thus α-dextrose is obtained by mixing a solution of 500 grms. of dextrose in 250 c.c. of water with 1000 c.c. of glacial acetic acid and leaving the mixture to stand at the ordinary temperature, the α-isomeride then slowly separating. The β-isomeride is obtained by mixing a hot solution of 500 grms. of dextrose in 50 c.c. of water with 600 c.c. of hot glacial acetic acid; the crystals which separate consist of β-dextrose to the extent of 93 per cent., and they may be further purified by solution in an equal weight of ice-cold water and precipitation with alcohol.

Dextrose, like many other sugars, exhibits the phenomenon known as mutarotation, i.e. the optical activity of the freshly prepared solution does not remain constant, but continues to change for several hours before it attains a fixed value; the change can be rendered almost instantaneous by boiling the solution or by adding a few drops of an alkali, *e.g.* ammonia solution. This phenomenon is due to the fact that dextrose is capable of existence in two isomeric forms, α-dextrose and β-dextrose, of different optical rotatory powers, and that when either form is dissolved in water it is slowly converted into the other until a certain state of equilibrium between the two is attained. The existence of these two forms of dextrose is best accounted for by the two following formulae:—



α-Glucose.



β-Glucose.

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[1] *J. Amer. Chem. Soc.*, 1917, **39**, 320.

in which the sugar is represented as containing a butylene oxide ring, the orientation of the terminal aldehyde group with regard to this ring being responsible for the $\alpha$- and $\beta$-isomers.[1] The specific rotatory powers of the isomers are: for $\alpha$-dextrose $[\alpha]_D = +111{\cdot}2°$ and for $\beta$-dextrose $[\alpha]_D = +17{\cdot}5°$. The proportion of the isomers in aqueous solution, when equilibrium has been attained, varies slightly with the concentration, so that the specific rotatory power of dextrose in aqueous solution is also dependent on concentration; it is expressed by the formula

$$[\alpha]_D = 52{\cdot}5 + 0{\cdot}018796p + 0{\cdot}00051683p^2,$$

in which p represents the weight of sugar in grams per 100 grms. of solution.[2] Hence, in 10 per cent. solution dextrose has a specific rotatory power of $[\alpha]_D = 52{\cdot}7°$, and the proportion of the $\alpha$-and $\beta$- isomers is 37·6 : 62·4.

If dextrose is crystallised from water at the ordinary temperature it separates in the hydrated form $C_6H_{12}O_6 + H_2O$, but at 35–40° C. it separates as the anhydrous sugar.

Anhydrous dextrose melts at 146–147° C.; the hydrated sugar has no definite melting point. Dextrose is readily soluble in water, 100 parts of which dissolve 81·68 parts of the sugar at 15° C.; it is only sparingly soluble in absolute ethyl alcohol and only slightly more soluble in absolute methyl alcohol.

Dextrose yields mannitol and sorbitol on reduction, whilst on oxidation it yields gluconic acid in the first instance. The conversion of dextrose into gluconic acid can be effected practically quantitatively by bromine or iodine in dilute alkaline solution and the reaction has been made the basis of a method for estimating dextrose.

If dextrose is treated with an equimolecular proportion of phenylhydrazine in presence of acetic acid it yields glucose phenylhydrazone (m.pt. 159–160° C.).

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[1] For a full account of recent views concerning the structure of dextrose, see E. F. Armstrong, "The Simple Carbohydrates and the Glucosides," 4th ed., 1924.

[2] Tollens, *Ber.*, 1884, **17**, 2234.

$$\underset{\text{Dextrose}}{CH_2OH.(CHOH)_4.CHO} + \underset{\text{Phenylhydrazine}}{H_2N.NH.C_6H_5} = \underset{\text{Dextrosephenylhydrazone}}{CH_2OH(CHOH)_4.CH{:}N.NH.C_6H_5} + H_2O$$

whilst if a considerable excess of phenylhydrazine is used, phenylglucosazone (m.pt. 205° C.) is formed.

$$CH_2OH.(CHOH)_4.CHO + 2(H_2N.NH.C_6H_5) = CH_2OH(CHOH)_3C{:}(N_2H.C_6H_5)CH.(N_2H.C_6H_5) + 2H_2O + 2H$$

Maltose may be prepared from starch by the action of barley diastase or malt diastase. According to J. L. Baker,[1] if soluble starch is treated with barley diastase at 50° C. for $1\frac{1}{2}$ hours, maltose and a dextrin are the sole products. If the solution is then treated with alcohol, the dextrin is precipitated in a flocculent state and the filtrate therefrom on evaporation to a syrup and treatment with strong alcohol yields crystallised maltose.

C. B. Duryea has proposed a process for obtaining maltose from starch in two stages, in the first of which (see p. 188) the starch is converted into a highly modified, thin-boiling form by treatment with acid. In the second stage[2] the highly modified starch, neutralised with alkali if necessary, is boiled, cooled to 59° C. and treated at about 58° C. for about 60 minutes with malt or malt extract in the proportion of about 5 lbs. of malt (dry basis) per 100 lbs. of the modified starch. The solution of maltose thus obtained is boiled, filtered and refined by the method previously described (see p. 203).[3]

M. Falch[4] has proposed the following method for preparing maltose on the laboratory scale:—A mixture of 300 grms. of potato starch and 1 litre of water is treated with 30 c.c. of malt extract (prepared by digesting 1 part of pale kilned or green malt with 4 parts of water for 3 hours), the whole being poured quickly into 2 litres of boiling water with stirring. The starch rapidly becomes liquefied and when the temperature has fallen to 60° C. a further portion of 30 c.c. of malt extract is added. The mixture is kept at 60° C. for 2 hours after it ceases to give a reaction with iodine, heated to boiling, filtered,

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[1] *Chem. Soc. Trans.*, 1902, **81**, 1177.

[2] E.P. 11,799 of 1907.

[3] F.P. 380,680, 1907.

[4] *Zeitsch. ges. Brauw.*, 1920, **43**, 281.

diluted to a sp. gr. of 1·028, treated with 240 c.c. of malt extract, and with hydrofluoric acid (7 mgrms. per 100 c.c.), and kept in a closed vessel for 3 days at 30° C., during which time no turbidity should appear. The solution is next treated with calcium carbonate, filtered, heated to boiling, and evaporated, preferably *in vacuo*, until its water-content is reduced to 30 per cent. The solution is then seeded with some crystals of maltose and kept at 40° C. to crystallise. If crystallisation is unduly slow, three portions of 70 c.c. of 90 per cent. alcohol are added at intervals of 1 day. The crystalline deposit is collected with the aid of a filter pump, then mixed with 90 per cent. alcohol and again collected. The product is then dissolved in water (30 c.c. per 100 grms.) on the water-bath, mixed with 90 per cent. alcohol (260 c.c.), heated to boiling and filtered. The filtrate, after cooling, is seeded with maltose and left to crystallise. It is stated that by this method 30 parts of pure maltose can be obtained from 100 parts of (air-dry) starch.

Maltose crystallises from alcohol (80 per cent.) with one molecule of water of crystallisation, which it does not lose readily even on heating *in vacuo*. Like dextrose, the sugar exists in $\alpha$- and $\beta$-forms; according to C. S. Hudson and E. Yanovsky[1], the rotatory powers of $\alpha$- and $\beta$-maltose are $[\alpha]_D = +158$ and $[\alpha]_D = +118°$ respectively. The rotation of the equilibrium mixture is, according to Brown, Morris and Millar,[2] $[\alpha]_D = +137·93°$ for aqueous solutions between 2 and 20 per cent. concentration at 15·5° C. (For the structural formula of maltose see p. 36.)

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[1] *J. Amer. Chem. Soc.*, 1917, **39**, 1013.

[2] *Chem. Soc. Trans.*, 1897, **71**, 109.

# CHAPTER XII.

# APPLICATIONS OF STARCH AND ITS PRODUCTS.

*Paper Making.*—Starch is used to a certain extent in the sizing of paper intended for printing or writing purposes, serving to harden and stiffen the material and improve its surface; it may be added directly to the pulp in the beaters or after admixture with the other constituents of the size. If the starch is added in the raw state to the pulp, it has no adhesive power and only acquires it when the paper passes over the hot drying cylinders, whilst if the starch is gelatinised before addition to the pulp, much of it becomes dissolved and lost. These difficulties may be partially overcome by using a mixture of raw and gelatinised starch, but according to H. Wrede,[1] a better method consists in using a mixture of starch and sodium silicate, which is heated with water until the mixture just begins to thicken. The mixture, after this treatment, is added to the pulp after the latter has been treated with size and alum; the starch and silicate are precipitated by the excess of alum, and the bulk of the starch is thus retained in the finished paper.

Starch, modified starch, and starch rendered soluble in cold water are used as adhesives in the manufacture of paste boards, and soluble starch is used in the preparation of surface-coated art papers.

*Textile Industry.*—Starch is used in large quantities as an ingredient of the size employed in treating cotton yarn before the latter is woven into cloth. The object of sizing the yarn is three-fold, viz., to bind loose hairs, to strengthen the yarn and to hold weighting materials such as china clay, etc.

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[1] *Wochenbl. Papierfabr.*, 1912, **43**, 1004; *Papier Zeit.*, 1913.

According to A. E. Owen,[1] sizing greatly increases the resistance of the yarn to variations in tension such as may be expected to occur in warp threads during weaving. It may be presumed that the strengthening effect of the starch on the yarn is chiefly dependent on the strength of the starch film itself. S. M. Neale[2] found that a starch film behaves very much like a ductile metal such as copper on loading and unloading and that there is scarcely any difference between the elastic properties of potato-, maize- and sago starches. The films are harder and more brittle in dry than in moist air. Weaker films are obtained if the starch has been oxidised with hypochlorite or otherwise more or less solubilised, and any admixture such as soap, glycerol, oils or fats tends to weaken the starch film although such admixtures may be desirable on other grounds.

According to the weight of size which it is desired to leave on the yarn, the sizing process may be classed as heavy (80 to 100 per cent.), medium or light (up to 20 per cent.) sizing.[3] In this country, wheat flour is most generally used for the preparation of size; according to P. Bean,[4] it is capable of adding as much as 40 per cent. to the weight of the yarn without the use of mineral matter or loss of weaving qualities. Prior to its use for sizing, wheat flour is either mixed with water and left to undergo prolonged fermentation or steeped in a solution of zinc chloride, being thus converted into a smooth size of great pliability. According to Bean,[5] potato starch is next in importance to wheat flour for sizing, being used chiefly in the sizing of goods of light reed and pick and giving for this class of work a smoothness and pliability to the yarn which is not excelled by any other starch. Potato starch paste loses its viscosity and adhesive power on protracted heating, but retains these properties if treated with a small proportion of sodium hydroxide. Sago starch is chiefly used in pure sizing; it strengthens the yarn more than any

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[1] *Shirley Institute Memoirs*, 1923, **2**, 263.

[2] *Ibid.*, 1924, **3**, 207.

[3] F. D. Farrow, *Shirley Institute Memoirs*, 1923, **2**, 194.

[4] *J. Text. Inst.*, 1915, **6**, 223.

[5] *Loc. cit.*

other starch used in sizing, and it stands prolonged boiling without losing strength; it requires to be well boiled, though less boiling suffices if a small quantity of sodium or potassium hydroxide is used in the mixing. Bean[1] states that tapioca starch is not often used for sizing, except for very light goods where a soft "feel" is desired; it may be used in conjunction with maize starch to take the place of potato starch. Maize starch is much used in America for light and medium sizing; it requires thorough boiling to prevent the size from being "dusted off" in the loom. Caustic alkali may be used with maize starch in pure sizing to effect complete gelatinisation of the starch granules. Maize starch is too harsh for heavy sizing, but it is valuable for this purpose if mixed with wheat flour.[2] According to F. D. Farrow,[3] size is commonly prepared as follows:—The dry starch is added to cold water in a beck, and the mixture agitated until all lumps are broken up. Steam is then admitted and fats and other ingredients are added when the mixture is hot, and boiling is continued until these are emulsified. If clay is a constituent of the mixture, it is boiled separately and the suspension is allowed to cool while under continual agitation. It is then run into the starch mixture and the whole is boiled well together with uninterrupted agitation. Bean has observed that since one of the objects of warp sizing is to strengthen the yarn, it is a mistake to use modified starches for this purpose except in very special cases where some particular effect is required; there appears to be no known process of modification whereby starch is rendered more suitable as a size than by merely boiling it.

Soluble starch, owing to the low viscosity of its solution, is of value in heavy sizing for thinning down the starch paste and rendering it easier to handle. The strong adhesive power of dextrin makes it useful as an adjunct to size to correct the loss of adhesiveness of the starch due to the presence of fat or oil.

Starch, soluble starch and dextrin are also used in the process of finishing cotton fabrics. The starches chiefly employed for this purpose are those of wheat, maize, potato,

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[1] *Loc. cit.*

[2] Bean, *ibid.*

[3] *Shirley Institute Memoirs*, 1923, **2**, 194.

cassava and rice, the usual procedure in preparing the finishing mixture consisting in heating a well-stirred mixture of the starch, mineral filler, etc., with water until the starch gelatinises. The starch serves to stiffen the cloth, to prevent "dusting out" of the filler during the beetling process, and to impart a gloss to the cloth if the latter is calendered. If the fabric is to remain soft, starch should not be used in the finishing process, but soluble starch or dextrin should be used instead. Soluble starch, like ordinary starch, produces a gloss on calendering, and it is also mixed with dextrin and a small proportion of ordinary starch for a soft finish. According to H. Pomeranz,[1] dextrin intended for cloth finishing should possess the following characteristics:—It should give a red-violet colour with iodine solution; the hot solution of the dextrin should remain clear on cooling except for a trace of flocculent matter; the sugar-content should preferably be 3–5 per cent., and never exceed 10–12 per cent.; the solution should not give more than a slight turbidity on treatment with a solution of tannin; the residue left on evaporating a solution should be glassy and give a solution similar to the original one, and cloth that has been dressed with the dextrin should show only a slight dampness in a moist atmosphere.

Starch and dextrin are widely used as "thickeners" in the colour-printing of cotton fabrics and other materials. In this process, the colours are printed on the cloth by means of engraved rollers and the starch or dextrin serves to increase the viscosity of the colour or mordant solution to such a degree that any running is prevented and a sharply defined impression is obtained. Wheat and maize starches are those most generally used as thickeners, and the latter is often admixed with a certain proportion of tapioca flour, a smoother paste being thus obtained; the starch is used at a concentration of 10–12 per cent., and it is frequently employed in conjunction with other thickening agents such as gum arabic and gum tragacanth. Dextrin is used as a thickener in 20–50 per cent. solution and is especially suitable for fabrics that are

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[1] *Monatschr. Textilind.*, 1922, **37**, 14.

required to have a soft finish. According to K. Gebhard,[1] starch greatly accelerates the rate of fading of colours, whereas dextrin retards fading; he therefore recommends the use of dextrin instead of starch in colour printing. P. G. Jones[2] has confirmed the observation that dextrin renders colours less liable to fade.

*Laundry Work.*—Starch is used in large quantities in laundries and in the household for dressing and finishing fabrics after washing. Wheat-, maize-, sago-, and rice starches, are employed for this purpose. To obtain the highly glazed surface required for collars, etc., the starch is mixed with a preparation known as starch glaze or starch gloss, which may consist of borax alone or of mixtures of various substances, including borax, French chalk, soap, stearin, white wax, paraffin wax, spermaceti, gum arabic, gum tragacanth, dextrin and glycerol. According to one recipe, 2 lb. of powdered tragacanth, 4½ lb. of spermaceti, and 18 lb. of borax are mixed with 1 cwt. of starch, whilst another recipe, for cold water starching, prescribes a mixture of 6 lb. of common salt, 6 lb. of powdered borax, 6 lb. of white dextrin, 9 lb. of rice starch and 22 lb. of sago flour.

S. B. Chambers[3] obtains a starch preparation suitable for laundry purposes by treating a mixture of 100 lb. of dry maize starch and 15 oz. of powdered borax with a solution of 6 oz. of nitric acid in 6 gallons of water; the mixture is left to stand for 24–48 hours, with occasional stirring to prevent any overheating, and then dried.

A laundry starch which is stated to render the fabric non-inflammable is prepared, according to J. Benoid,[4] by mixing sodium tungstate, magnesium sulphate, magnesium carbonate, borax, sodium thiosulphate and sodium bicarbonate with maize- or rice flour. A preparation for the same purpose claimed by H. Becker[5] consists of starch, aluminium sulphate, ammonium phosphate, ammonium chloride and ammonium sulphate.

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[1] *J. Soc. Dyers & Col.*, 1909, **25**, 306.

[2] *Ibid.*, 1910, **26**, 147.

[3] U.S.P. 1,276,722, 1918.

[4] E.P. 14,205 of 1906.

[5] E.P. 20,460 of 1906.

*Leather Industry.*—Glucose is used as an ingredient of bating and puering liquors in leather manufacture, and starch paste is used as a vehicle for the tanning extract in drum tannage. A. Turnbull and T. B. Carmichael[1] have devised a process according to which starch is added to the tanning liquor and the mixture is heated to 82° C. to effect gelatinisation of the starch, and then cooled; this addition of starch is said to render the liquid more capable of penetrating the pelt or hide and to improve the quality of the leather.

*Confectionery Purposes.*—Cereal flours and starches are largely used in the manufacture of custard powders, ice cream powders, cake powders, etc., and the following are some recipes:—

Custard Powder.—Coloured cornflour (for preparation, see below), 33 lb.; cornflour, 576 lb.; fine rice flour, 6 lb.; sago starch, 54 lb.; salt, 3 lb.; natural vanilla essence, 1 lb. 3 oz.; lemon essence, 9½ oz.

Sweetened Custard Powder.—Coloured cornflour, 22 lb.; cornflour, 390 lb.; rice flour, 8 lb.; sago starch, 32 lb.; salt, 4 lb.; fine sugar, 320 lb.; saccharin, 8 oz.; natural vanilla essence, 1 lb. 2 oz.; almond essence, 2 oz.

Coloured Cornflour for colouring Custard Powder, etc.—A solution of 375 grms. Egg Yellow aniline dye and 40 grms. Orange I in half a gallon of water is thoroughly mixed with 60 lb. dry cornflour, the mixture then being made up to 600 lb. with additional cornflour.

Cake Mixture.—Patent grade wheat flour, 380 lb.; castor sugar, 240 lb.; acid calcium phosphate of acidity equal to that of cream of tartar, 15 lb.; sodium bicarbonate, 7½ lb.; potato starch, 1½ lb.; cornflour, 1½ lb.; salt, 1½ lb.; coloured cornflour (see above), 3½ lb.; natural vanilla essence, 1 lb.

Sponge Cake Mixtures.—First packet: dry flour, 300 lb.; powdered sugar, 300 lb.; coloured cornflour, 2 lb.; rice flour, 32 lb.; potato starch, 10 lb.; cream of tartar, 29 lb.; flavours, according to requirements. Second packet: flour, 310 lb.; powdered sugar, 305 lb.; rice flour, 32 lb.; sodium bicarbonate, 26½ lb..

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[1] E.P. 110,470, 1917.

Gravy Salt.—Sago starch, 56 lb.; salt, 28 lb.; yeast extract or meat extract, 10 lb.; liquid caramel, 8½ lb.

Ice Cream Powder.—Castor sugar, 332 lb.; cornflour, 16 lb.; gum tragacanth, 12 lb.; coloured cornflour, 6 lb.; saccharin, 2 oz.; natural vanilla essence, 3 lb. 12 oz. This preparation is made without cooking; some ice cream powders, similar to sweetened custard powders, require cooking.

*Pharmaceutical and Toilet Purposes.*—Wheat-, maize- and rice starches are specified in the official list of the British Pharmacopoeia, whilst only maize starch is specified in that of the American Pharmacopoeia.

Maize starch is employed as principal ingredient of violet and dusting powders, arrowroot starch, finely sifted and tinted, is used as theatrical face powder, whilst rice starch is the most important constituent of Poudre de Riz or face powder. Potato starch is not much used for toilet purposes, as the granules are so large as to be almost visible to the eye. Poudre de Riz of the best quality contains 50 per cent. of rice starch or more, and may contain maize starch as well, whilst in preparations of inferior quality, maize starch may be the principal ingredient. In addition to these starches, face powders commonly contain other substances such as zinc oxide, magnesium or zinc stearate, talc, orris root powder, magnesium or calcium carbonate, kieselguhr or kaolin.

The preparation known as glycerate of starch or glycerin of starch is obtained, according to the British Pharmacopoeia, by heating a mixture of 20 grms. starch, 130 c.c. glycerol and 30 c.c. distilled water, with constant stirring until a translucent jelly is obtained. The product is used alone or admixed with zinc oxide as a cosmetic cream, and it is also used in the preparation of liniments and pomades.

*Miscellaneous Applications.*—Messrs. Courtauld's Ltd., W. H. Stokes and J. A. Lloyd,[1] treat starch with sulphuric acid in order to obtain solutions suitable for the preparation of, or for addition to a setting back for use in the manufacture of threads, filaments, strips or films from viscose.

Starch is sometimes used, in conjunction with potassium

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[1] E.P. 181,197 and 181,198, 1921.

silicate, as a "filler" in soft soaps, but it cannot be regarded as other than an adulterant since it has no detergent power.

L. Marton[1] has proposed to use starchy materials and waste products as cementing agents in the manufacture of fuel briquettes, but briquettes so prepared are liable to disintegration when moistened unless treated with a waterproofing agent in addition

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[1] E.P. 21,755 of 1904.

# CHAPTER XIII.

# ANALYSIS.

## ANALYSIS OF STARCHES AND AMYLACEOUS MATERIALS.

The analysis of commercial starches may comprise estimations of water, mineral matter, protein, starch and occasionally fat and fibre. Since these constituents make up the whole of the material, the percentage of starch in commercial starches may be found indirectly by estimating the percentages of the other constituents and deducting their sum from 100. Otherwise, the starch may be estimated directly by one of the methods described on pp. 222–228. In the case of other starchy materials, of course, one of the direct methods of estimation must be employed.

*Water.*—Air-dried starch retains a considerable proportion of moisture, e.g. about 13 per cent. in the case of wheat starch and as much as 18–20 per cent. in the case of potato starch.

Water in starch or starchy material may generally be accurately determined by the loss in weight on direct heating. Since, however, starch is gelatinised by water at a temperature (55–80° C.) far below that at which the water is completely expelled, the bulk of the water must be removed at a temperature below the gelatinising point, the material, thus partially dried, then being heated sufficiently to expel the whole of the remaining water. The procedure consists in heating 10 grms. of the starch at 45–50° C. for 1 hour and then at 120° C. for 4–6 hours.

Saare[1] has described a rapid method for estimating water in potato starch, more especially intended for purposes of factory control, the results usually being accurate to within

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[1] *Zeitsch. Spiritusind.*, 1884, 7, 550.

0·5 per cent.; the method is based on the fact that the specific gravity of anhydrous potato starch is 1·65. One hundred grms. of the starch are mixed with distilled water to a uniform fluid suspension which must be free from lumps. The suspension is transferred quantitatively to a weighed 250 c.c. flask, made up to volume at 17·5° C. and weighed. If W is the weight of the contents of the flask in grms., the water-content of the starch is found from the formula:—

$$\text{Percentage of water} = \frac{289{\cdot}4 - W}{0{\cdot}394}$$

The weighings should be made as accurately as possible, since a difference of 0·1 in the value of W corresponds to a difference of 0·25 per cent. of water.

*Mineral Matter.*—The mineral matter in starch is determined by igniting 5 grms. of the sample in a muffle furnace until the residue is white or, at most, of a light grey colour.

The mineral-content of high-grade commercial potato starch may range from 0·2 to 0·4 per cent. (referred to dry substance), but is rather less—0·13 per cent. on the average—in wheat and maize starches; about one-half of the mineral matter consists of phosphoric acid. H. Tryller[1] has observed that the lime present in ordinary potato starch is derived almost entirely from the water used in manufacture by exchange for potash originally present in the starch.

*Protein.*—The amount of protein is found by multiplying the percentage of nitrogen by the factor 6·25, the nitrogen being estimated by Kjeldahl's well-known method.

*Fat.*—Fat may be estimated by extracting a weighed and dried portion of the starch with ether or petroleum ether in a Soxhlet extractor. Since the amount of fat is generally very small, as large a quantity of the starch as practicable should be taken for analysis.

According to T. C. Taylor and J. M. Nelson,[2] maize starch, in addition to any extraneous fat, contains a small proportion of fatty matter which must be combined in some way with the starch since it is not removable by solvents and is only

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[1] *Chem. Zeit.*, 1920, **44**, 833.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 1726.

set free, in the form of palmitic and other fatty acids, when the starch is hydrolysed; other starches, too, contain small proportions of combined fatty matter, viz. maize starch, 0·61; rice starch, 0·83; sago starch, 0·11; cassava starch, 0·12; potato starch, 0·04; and horsechestnut starch, 0·56 per cent. Taylor and L. Lehrmann[1] found that the combined fatty acids set free when maize starch is hydrolysed consist of about 24 per cent. of palmitic, 40 per cent. of oleic and 36 per cent. of linolic acid. Since these fatty substances are not extracted by fat solvents they would not, of course, be included in the amount of fat found by the method described above; this exclusion is justifiable, if, as is considered by Taylor and Lehrmann, these fats are combined with the amylopectin constituent of the starch (see p. 203).

*Starch.*—The estimation of starch in the various plant materials and products in which it occurs has been the subject of much investigation and numerous methods for this purpose have been devised, some of them applicable to amylaceous materials in general and others designed to meet the requirements of special cases. In most of the methods the starch is hydrolysed to a greater or less degree and the product—reducing sugar or soluble starch—is determined by copper reduction or polarimetrically. In what follows, methods depending on hydrolysis and copper reduction are first described and then those depending on solubilisation and polarisation.

### *Methods depending on Hydrolysis of the Starch to reducing Sugar and estimation of the latter by Copper reduction.*

*Method of Direct Acid Hydrolysis.*—This method is one of those adopted in America by the Association of Official Agricultural Chemists; it is open to the objection that it includes as starch any pentosans or other carbohydrate bodies that undergo hydrolysis on treatment with acid.

A weighed quantity of the sample representing 2·5–3 grms. of dry material is stirred in a beater with 50 c.c. of cold water

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[1] *J. Amer. Chem. Soc.*, 1926, **48**, 1739.

for an hour. It is then transferred to a filter and washed with 250 c.c. of cold water. The insoluble residue is heated for 2½ hours with 200 c.c. of water and 20 c.c. of dilute hydrochloric acid (sp. gr. 1.125) in a flask with reflux. The solution is then cooled, nearly neutralised with sodium hydroxide, made up to 250 c.c. and filtered. An aliquot portion of the filtrate is used for the determination of dextrose (see pp. 235–244). The amount of dextrose found, multiplied by 0·90, gives the corresponding weight of starch.

*Maercker's Method.*—Three grms. of the finely ground material (previously extracted with ether to remove fat if necessary) are heated with 100 c.c. of water in a boiling water-bath for half an hour, cooled to 65° C., and treated at this temperature for about 2 hours with 10 c.c. of malt extract (prepared by extracting 100 grms. of ground malt with 1 litre of water for 2 hours and then filtering until clear), heated in a boiling water-bath again for half-an-hour, cooled to 65° C., and treated at this temperature with 10 c.c. of the malt extract for half an hour, boiled again, cooled to room temperature, made up to 250 c.c. and filtered. Two hundred c.c. of the filtrate are heated with 15 c.c. of 25 per cent. hydrochloric acid (sp. gr. 1·125) in a flask in a boiling water-bath for 2½ hours, cooled, neutralised and made to a suitable volume. The dextrose is estimated by one of the methods described on pp. 235–244, and its amount, multiplied by 0·90, gives the corresponding weight of starch.

A blank experiment must be made with the malt extract, which is heated with hydrochloric acid under the prescribed conditions, and the reducing power of the main solution corrected for that of the malt extract.

C. J. Lintner has shown that in the case of materials, such as cereals, containing more than a small proportion of pentosans, the results obtained by the above method are liable to be higher than the true value, though not so high as those obtained by acid hydrolysis. Moreover, cereal grains, and especially malted grains, contain appreciable amounts of ready-formed sugars which are included as starch when the latter is estimated by the above method. For many of the purposes for which the estimation of starch in cereals is required, the ready-formed sugar is as valuable as the starch, and there is no practical objection to its inclusion. For the accurate estimation of starch actually present as such in raw or malted cereals (barley and malt), H. T. Brown[1] has proposed the following method.

*Brown's Method.*—A weighed quantity of the finely ground material (about 5 grms.) is extracted with 80 c.c. of alcohol of sp. gr. 0·920, for which purpose, according to A. R. Ling and W. J. Price,[2] the ordinary form of Soxhlet extractor serves very well. The extraction is continued for 3 hours in the case of barley, or 9 hours in the case of malt, by which time the whole of the reducing substances and alcohol-soluble nitrogen compounds are removed.

The contents of the thimble are then placed in a beaker containing about 100 c.c. of water, and boiled thoroughly, cooled to 57° C., and treated with 10 c.c. of an active malt extract. The latter is prepared by extracting 100 grms. of finely ground malt (of diastatic power, 80, on the Lintner scale), with 250 c.c. of water at 15–20° C. for 2 hours and filtering.[3] The conversion is allowed to proceed at 57° C. for 60 minutes, the solution then being boiled, filtered into a 200 c.c. flask, the residue well washed and the volume of the filtrate made to 200 c.c. after cooling. The maltose-content of an aliquot portion of the solution is then determined by one of the methods given on pp. 235–244. A correction of course must be made for the reducing power of the malt extract, and, according to Ling and Price,[4] a volume of the extract equal to that employed in the saccharification and diluted to the same extent with water should be heated side by side with the solution of the sample. The amount of maltose formed having been ascertained, the starch equivalent to this maltose is calculated from the equation

$$10C_{12}H_{20}O_{10} + 8H_2O = 8C_{12}H_{22}O_{11} + 2C_{12}H_{20}O_{10}$$

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[1] *Guinness Research Lab. Trans.*, 1903, **1**, 79.

[2] *J. Inst. Brew.*, 1922, **28**, 851.

[3] Brown and Heron, *Chem. Soc. Trans.*, 1879, **35**, 601.

[4] *Loc. cit.*

(see p. 18), according to which 84·4 parts of maltose correspond to 100 parts of starch. According to Brown, this proportionality holds if the malt from which the extract used for saccharification is prepared, has a diastatic power of 80 (Lintner); if, however, an ordinary kiln-dried malt of diastatic power 40 is used, only 82·5 parts of maltose are obtained, whilst with a low-dried malt of very high diastatic power, more than 84·4 parts of maltose are obtained. Ling and Price[1] propose to avoid the limitation to malt of d.p. 80 by means of the formula:

$$S = \frac{94{\cdot}73M'}{M}$$

in which S is the percentage of starch in the sample, M the percentage of apparent maltose produced from dry barley- or wheat starch by the action of malt extract prepared from malt of a definite diastatic power, and M′ the percentage of apparent maltose produced from the sample under the same conditions and with malt of the same diastatic power.

### *Polarimetric Methods.*

Several methods of estimating starch by solution of the material in acid and determination of the rotatory power of the solution have been proposed, of which one, devised by C. J. Lintner[2] for the estimation of starch in barley is as follows: Five grms. of the very finely ground cereal are triturated with 20 c.c. of water until free from lumps and then mixed with 40 c.c. of concentrated hydrochloric acid (sp. gr. 1·19), the mixture being allowed to stand for 30 minutes, by which time it is converted into a dark coloured, mobile liquid. The solution is rinsed into a 200 c.c. flask with hydrochloric acid of sp. gr. 1·125, treated with 10 c.c. of a 4 per cent, solution of phosphotungstic acid and made to 200 c.c. with hydrochloric acid of sp. gr. 1·125. The solution is then mixed and filtered through a pleated filter the end of which is strengthened with a small smooth filter. The angular rotation of the clear filtrate is read in a 200 m.m. tube with sodium light. The starch-content of the barley is calculated on the assumption

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[1] *Loc. cit.*

[2] *Zeitsch. ges Brauw.*, 1907, **30**, 109.

that barley starch dissolved in hydrochloric acid under the prescribed conditions has $[\alpha]_D^{20} = 200{\cdot}3°$, the amount of starch in the sample being found from the formula:

$$\text{Percentage} = \frac{4000\,a}{l[a]_D}$$

in which $a$ = the observed angular rotation, $l$ = length of polarisation tube in decimetres and $[a]_D$ = specific rotatory power of barley starch under the conditions given.

M. Canet and O. Durieux[1] found that the above method is applicable to cereals and amylaceous materials in general, but they prefer the value $[a]_D^{20} = 202°$ for calculating the percentage of starch. O. Wenglein[2] modified the method by using sulphuric instead of hydrochloric acid for dissolving the starch.

Instead of the cold, comparatively concentrated acids used by Lintner and Wenglein for effecting solution of the starch, E. Ewers[3] uses hot dilute hydrochloric acid as solvent in estimating starch in barley; his procedure is as follows:—Five grms. of the very finely ground material are thoroughly shaken with 25 c.c. of dilute hydrochloric acid (containing 1·124 per cent. of hydrochloric acid by weight) in a 100 c.c. flask, the neck of the flask being washed down with a further quantity of 25 c.c. of the same dilute acid. The flask is again shaken several times and then heated in a boiling water-bath for exactly 15 minutes, during the first three of which it is repeatedly rotated. The contents of the flask are then made up to about 90 c.c. with cold water, treated with 2 c.c. of sodium molybdate solution (prepared by fusing 30 grms. molybdic acid with 25 grms. dry sodium carbonate, dissolving the product in water to 250 c.c. and filtering) or with 10 c.c. of a 4 per cent. solution of phosphotungstic acid, made up to 100 c.c. with water, mixed, filtered and polarised in a 200 mm. tube. The specific rotation of barley starch under these conditions is $[a]_D^{20} = 181{\cdot}5°$. If a saccharimeter is used, the percentage

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[1] *Bull. Soc. chim. Belg.*, 1907, **21**, 329.

[2] *Zeitsch. ges. Brauw.*, 1908, **31**, 53; cp. also C. J. Lintner, *Zeitsch. angew. Chem.*, 1912, **25**, 1177.

[3] *Zeitsch. ges. Brauw.*, 1908, **31**, 250.

of starch in the sample is obtained by multiplying the Ventzke reading by 1·912. After reading, the solution may be treated with a few drops of molybdate solution to make sure that all the protein has been precipitated. The starch solutions obtained by this method show no decrease of rotation in 24 hours. A slightly modified method, for the estimation of starch in potatoes, has also been described by Ewers.[1]

J. König, W. Greifenhagen and A. Scholl[2] have determined the specific rotatory powers of the more important starches dissolved in hydrochloric acid according to Lintner's method (see p. 225) and in hot dilute hydrochloric acid according to Ewers' method (see p. 226). In calculating these figures the percentages of starch in the starches used were estimated both by difference (i.e. 100 minus the sum of the percentages of the other constituents) and by hydrolysis with acid to dextrose and estimation of the latter. The results are shown in Table X; the figures for banana starch are due to G. Baumert.[3] Table X shows that Ewers' method gives considerably lower rotations than those obtained by Lintner's method, owing no doubt to greater hydrolysis of starch in the former. Further, the rotations calculated on the percentages of starch estimated by difference are in all cases lower than those calculated on the percentages estimated by hydrolysis; the figures based on hydrolysis are considered more accurate since the others may be vitiated by the presence of undetermined non-nitrogenous organic substances in the starches. A mean value of $[\alpha]_D = 202°$ for starch dissolved by Lintner's method would be sufficiently accurate for most of the commoner starches. The rotations determined by Ewer's method vary much more with the different starches and a mean value could not be used for all without serious error in some cases; for maize, rice, wheat, rye, barley and oat starches, the mean specific rotation may be taken as 183·7 (by difference) or 184·9 (by hydrolysis). With feeding stuffs and other amylaceous materials containing optically active substances besides starch, the former should be removed by

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[1] *Zeitsch. öffentl. Chem.*, 1915, **21**, 232.

[2] *Zeitsch. Nahr.-Genussm.*, 1911, **22**, 714.

[3] *Ibid.*, 1912, **24**, 449.

washing a weighed quantity of the material in an asbestos-packed Gooch crucible with cold water, alcohol and ether. The starch and asbestos are then transferred to a 100 c.c. flask, and further treated according to Lintner's or Ewer's method; it is stated that cellulose, hemicellulose and pentosans do not affect the accuracy of the results obtained by either method.

TABLE X.

| Kind of Starch. | $[\alpha]_D$ Lintner. Starch estimated by. | | $[\alpha]_D$ Ewers. Starch estimated by. | |
|---|---|---|---|---|
| | difference. | hydrolysis. | difference. | hydrolysis. |
| Potato | 201·2 | 204·5 | 191·8 | 195·0 |
| Maize | 201·2 | 205·2 | 182·5 | 186·2 |
| Rice | 200·8 | 203·2 | 185·8 | 188·0 |
| Wheat | 200·3 | 203·8 | 182·7 | 185·9 |
| Rye | 200·4 | 205·8 | — | 182·9 |
| Barley | 198·2 | 205·5 | 180·0 | 186·7 |
| Oat | 193·2 | 201·8 | — | 180·0 |
| Millet | 183·7 | 201·2 | — | 165·5 |
| Bean | 204·6 | 208·3 | 169·4 | 172·4 |
| Lentil | 195·8 | 204·8 | 181·3 | 185·4 |
| Pea | 198·0 | 201·0 | 185·0 | 187·8 |
| Buckwheat | 199·6 | 201·6 | 170·0 | 171·7 |
| Arrowroot | 198·6 | 201·9 | 182·9 | 185·9 |
| Maranta | 204·7 | 212·7 | 177·4 | 184·3 |
| Palm Sago | 202·6 | 209·6 | 180·3 | 186·5 |
| Tapioca | 203·9 | 210·9 | 181·5 | 187·7 |
| Pepper | 201·9 | 207·8 | 179·2 | 184·5 |
| Banana | 209·8 | — | 196·4 | — |

C. Mannich and K. Lenz[1] describe a method for the polarimetric estimation of starch in which solution of the starch is effected by boiling with a concentrated solution of calcium chloride rendered faintly acid (1/1000–1/500$N$) with acetic acid; this slight acidity is stated to prevent the boiled solution from becoming turbid on cooling.

J. C. Small has devised a method for estimating soluble starch in presence of starch and its hydrolytic cleavage products for which the reader is referred to the original.[2]

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[1] *Zeitsch. Nahr.-Genussm.*, 1920, **40**, 1.

[2] *J. Amer. Chem. Soc.*, 1919, **41**, 107.

## ANALYSIS OF STARCH DEXTRIN.

*External Appearance.*—Dextrins made by heating with acids are generally of a white, cream or yellow colour, whereas those made by roasting without acid are usually brownish. Coloured dextrins are almost completely soluble in both hot and cold water, but white dextrins are more or less insoluble in cold water. Potato starch of high quality yields very lustrous dextrin, inferior potato starch yields moderately lustrous dextrin, whilst the dextrins made from wheat and maize starches have a matt appearance.

*Odour and Flavour.*—Pure dextrin is almost odourless when dry, but acquires a characteristic odour when moistened or dissolved. With long experience it is possible to judge from the flavour whether the dextrin has been prepared by acid treatment and even to distinguish the acid used. The degree of sweetness affords some indication of the sugar-content.

*Texture.*—The texture or "feel" of the sample permits of the detection of hard particles, lumps, etc. Dextrins made from cereal starches are soft to the touch and tend to adhere to the dry hand; those from potatoes always feel somewhat harsh and are less adherent.

*Microscopic Appearance.*—In the case of powder dextrin microscopical examination shows the origin, since the dextrin retains the structure of the starch granules more or less unchanged; it is even possible to decide whether one or more starches have been used in manufacture.

*Water.*—For powder dextrins 10 grms. of the sample are heated for 4 hours at 105° C. With granulated and liquid dextrins, a solution of 2 grms. in a small quantity of water is poured into a weighed dish of ignited sand provided with a glass stirring rod. After careful mixing, the whole is heated first on a water-bath and then for 4 hours at 100° C. Powder dextrins usually contain 8–11 per cent. of water though freshly prepared dextrins may contain less.

*Acidity.*—One hundred grms. are dissolved in 5–10 times the quantity of warm water, cooled and titrated with $N/1$ sodium hydroxide; the acidity should not exceed 5 c.c. of

$N/1$ solution. It should be pointed out that the degree of acidity does not afford evidence as to whether the dextrin has been prepared by the acid process.

*Mineral Matter and Sand.*—Ten grms. of the sample are incinerated in a platinum or porcelain dish; if any carbonaceous residue remains, it should be moistened with a drop or two of ammonium nitrate solution, and again ignited. The sand may be estimated by dissolving the ash in distilled water and weighing the residue. High class dextrins should not contain more than 0·5 per cent. of mineral matter including 0·2 per cent of sand.

*Portion Soluble in Cold Water.*—The following method, described by F. Lippmann,[1] is accurate and expeditious:—Twenty grms. of the sample are treated with 200 c.c. of water in a flask of about 500 c.c. capacity. To effect more rapid solution it is advisable to pour 100 c.c. of water into the flask and then add the weighed quantity of dextrin, the flask being shaken during this addition, and finally add the remaining 100 c.c. of water. The flask is then tightly stoppered and vigorously shaken for a shorter or longer period according to the greater or less solubility of the sample; five minutes suffices in most cases. The solution is next filtered through a dry pleated filter and the density of the filtrate determined with a Brix hydrometer; the reading, multiplied by 10, gives the percentage of the portion soluble in cold water.

*Portion insoluble in Cold Water.*—This is found by deducting the percentage of the portion soluble in cold water from 100.

*Portion soluble in Hot Water.*—This estimation is rarely required since dextrins are or should be almost completely soluble in hot water. A qualitative test, made by boiling a small portion of the sample with water in a test tube is generally sufficient.

*Dextrin.*—That portion of commercial dextrin which is soluble in cold water contains dextrose and soluble salts in addition to dextrin. The percentage of dextrin, or more strictly, of non-reducing organic substances, is found by estimating the reducing sugar and ash in the portion soluble

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[1] *Zeitsch. Spiritusind.*, 1902, **25**, 237.

in cold water; the difference between their sum and the portion soluble in cold water represents the dextrin.

*Soluble Starch.*—In the case of dextrins free from unaltered starch, the portion insoluble in cold water consists almost entirely of soluble starch, so that further examination of this portion is usually unnecessary. The proportion of soluble starch is also represented by the difference between the portions soluble in hot and in cold water.

*Unaltered Starch.*—Commercial dextrin should be, and generally is, free from unaltered starch but the latter may be present either as an intentional addition, or owing to imperfect dextrinisation. It may be detected by the gelatinisation that occurs when the sample is boiled with water or by treating the sample with sodium hydroxide solution with which it gives a viscid paste. The iodine reaction of starch-containing dextrin is of course blue or blue-black. The amount of unaltered starch is found by hydrolysing the residues from both the cold water soluble- and the hot water soluble portions, to dextrose. The dextrose derived from the residue from the hot water soluble portion corresponds to unaltered starch whilst the difference between the amounts of dextrose derived from the two residues corresponds to soluble starch.

*Sugar.*—Sugar is best estimated volumetrically with Fehling's solution, using methylene blue as internal indicator (see p. 239). The sugar in commercial dextrin consists chiefly of dextrose and it is best to return the reducing sugar found in terms of dextrose, but it should be borne in mind that it may consist in part of maltose and that the various dextrins themselves do not appear to be entirely devoid of reducing power (see p. 191).

*Chlorine.*—Free chlorine or hypochlorous acid renders dextrin unsuitable for many purposes. A qualitative test by the usual well-known methods suffices; the presence of chlorine may be due to the use of starch that has been bleached with chlorine or hypochlorous acid or to one of the processes for making dextrin in which chlorine or ozone is used.

*Gluten.*—Dextrin prepared from wheat starch may contain hard particles of roasted gluten which render it unsuitable for some purposes. To detect burnt gluten, 1 part of the sample is stirred with 1 part of water at 60° C., the solution thus obtained being mixed with 5 parts of water at the same temperature. The mixture is left for 24 hours during which time the burnt gluten swells, and without dissolving or rendering the solution viscous, settles to the bottom of the vessel.

*Iodine Reaction.*—This reaction affords some guidance to the degree of dextrinisation of the starch and O. Saare[1] has proposed the following procedure for factory control:—0·1 grm. of the sample is mixed with 5 c.c. water in a large test tube marked at 100 c.c., heated until the material is dissolved, and diluted to 100 c.c. with cold water. The solution is then treated with 1 drop of $N/10$ iodine and the colours produced as the drop falls and after shaking noted. Table XI shows the nature of the colour change and degree of dextrinisation in one series of tests.

TABLE XI.

| No. | Falling Drop. | After Shaking. | Percentage of water-soluble part referred to anhydrous material. |
|---|---|---|---|
| 1 | Blue. | Blue. | 0 |
| 2 | Blue. | Pale blue. | 6·1 |
| 3 | Blue-violet | Pale blue. | 15·2 |
| 4 | Violet. | Violet. | 39·2 |
| 5 | Violet-red | Pale violet. | 49·5 |
| 6 | Reddish-brown. | Colourless. | 62·5 |

The table would not of course be applicable to all cases and it is advisable, in applying the test, to compile a table from actual results for each method of manufacture. At best, the test can only afford a rough indication of the degree of dextrinisation and it suffers from the serious defect that the colours with dextrins of high solubility—70 to 90 per cent.—show scarcely any differences.

*Consistency and Stability.*—Since the various substances comprised under the name dextrin differ so widely in chemical and physical properties, it is not surprising that samples prepared from similar raw materials and similar as regards

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[1] *Zeitsch. Spiritusind.*, 1900, **23**, 53.

appearance, acidity, cold water solubility, etc., may show great differences in those properties for which dextrin is chiefly valuable. Mere concordance of the results of analysis of two samples of dextrin does not guarantee their similarity. Hence, the examination of dextrin for consistency, stability and viscosity of its solution is of the utmost value for factory control and for matching samples, the value of a dextrin being largely dependent on these properties.

Comparative tests of consistency are made by boiling 30 grms. of each sample with 30 c.c. water in porcelain dishes over a direct flame with continuous stirring until the solutions are perfectly homogeneous. The solutions, after cooling, are compared in respect of consistency, adhesiveness, ropiness, etc.

For comparison of stabilities, the solutions prepared as just described are left for several days in a germ-free atmosphere Whilst many dextrins soon dry, exhibit surface cracks and lose their elasticity and tenacity or stringiness, others remain unchanged for several days; the more stable kinds are specially to be preferred for use with dyes and for textile purposes.

*Viscosity.*—This test, like those for consistency and stability, is especially valuable for comparing or matching samples; it may be made on the solutions prepared both with cold and hot water though the latter is seldom required. The cold water solution is prepared by shaking 10 grms. of the sample with 50 c.c. water until solution of the soluble part is complete. The solution is filtered through a dry filter and the viscosity of the filtrate determined at a standard temperature. Engler's viscometer may be used for this determination, but for purposes of comparison and factory control determinations of the rate of flow of the solution from any graduated tube are often sufficient. If the hot water solution is required it should be prepared by boiling the sample with water and then cooling to the standard temperature. The determination of viscosity is of especial value for discriminating between coloured dextrins; such products are generally almost completely soluble both in hot and cold water and cannot, therefore, be distinguished by determinations of solubility.

## ANALYSIS OF STARCH SUGAR.

The term "starch sugar" comprises commercial glucoses of various qualities such as pure dextrose, solid glucose or grape sugar, which, in addition to the main constituent, dextrose, may contain maltose, dextrin, protein, mineral matter and water, and glucose syrup or corn syrup which generally contains larger proportions of the subsidiary constituents than the solid forms of the sugar. Full analysis of a starch sugar or syrup includes estimations of dextrose, maltose, protein, mineral matter and water, the unfermentable matter (gallisin and dextrin) being found by difference.

In commercial glucoses, the dextrose may range from about 50 to 75; maltose, 2 to 12; unfermentable matter, 10 to 15; mineral matter, 0·5 to 2, and protein, 0·2 to 2 per cent. Glucose syrups generally contain much smaller proportions of dextrose and larger proportions of maltose and unfermentable matter than the solid sugars.

*Water.*—In the case of solid starch sugar products which do not contain enough water to cause appreciable melting on heating, water may be determined by heating 5 grms. sample at 100–105° C., for 2 hours, cooling and weighing, heating again for 1 hour and, if necessary, for a further period until a constant weight is attained.

With materials containing so much water that they run or melt on heating, the whole of the water cannot be expelled in this way. For such materials and for syrups, a method known as the solution density method is rapid and sufficiently accurate for most purposes; it depends on the facts that aqueous solutions of different carbohydrates of equal concentrations possess nearly equal specific gravities and that the difference between the specific gravity of a carbohydrate solution and that of water is nearly proportional to the concentration of the carbohydrate. If the excess density of a 10 per cent. carbohydrate solution over that of water at 15·5°/15·5° (water being taken as 1000) is divided by 3·86, the quotient represents the carbohydrate concentration of the solution in grms. per 100 c.c. The divisor 3·86 is also sufficiently accurate for the other constituents of starch sugar and syrup excepting the mineral matter which has a divisor of about 8 (i.e., a 1 per cent. solution has a sp. gr. of about 1008). Hence in determining water by the solution density method, the percentage of soluble ash in the sample must be multiplied by 0·8 and the product subtracted from the specific gravity of the 10 per cent. solution of the sample at 15·5/15·5°. The remainder represents the sp. gr. of the 10 per cent. solution due to organic solids and this figure less 1000, divided by 3·86 gives the percentage of organic solids in the 10 per cent. solution, and this multiplied by 10, gives the percentage of organic solids in the sample. The percentage of water is found by deducting the sum of the organic solids and ash from 100.

*Example.*—A starch syrup contained 0·65 per cent. ash, and its 10 per cent. solution (10 grms. dissolved in water and made to 100 c.c.) had sp. gr. 15·5/15·5 = 1031·77.

$$\text{Percentage of organic solids} = \frac{\{1031{\cdot}77 - (0{\cdot}65 \times 0{\cdot}8)\} - 1000}{3{\cdot}86} \times 10 = 80{\cdot}95$$

$$\text{Percentage of total solids} = (80{\cdot}95 + 0{\cdot}65) = 81{\cdot}6.$$

$$\text{Percentage of water} = (100 - 81{\cdot}6) = 18{\cdot}4.$$

Another method of estimation is that described for granulated and liquid dextrins on p. 229.

*Ash.*—Five grms. of sample are moistened with about 1 c.c. sulphuric acid, heated, gently at first and then at low redness, until completely burnt, one tenth being deducted from the weight to allow for "sulphating."

*Protein.*—See p. 221.

*Dextrose, Maltose and unfermentable matter.*—These are best estimated according to a scheme devised by G. H. Morris.[1] Ten c.c. of the 10 per cent. solution used in the determination of water by the solution density method are diluted to 50 c.c. of which 10 c.c. (= 0·2 grm. sample) are used for the determination of reducing power by Brown, Morris, and Millar's method[2] thus:—Fifty c.c. of Fehling's solution (made by

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[1] *J. Inst. Brew.*, 1898, **4**, 162.

[2] *Chem. Soc. Trans.*, 1897, **71**, 94.

mixing equal volumes of a solution containing 34·6 grms. crystallised copper sulphate, $CuSO_4, 5H_2O$ per 500 c.c., and a solution containing 173 grms. Rochelle salt and 65 grms. sodium hydroxide per 500 c.c.) are transferred to a beaker flask of about 250 c.c. capacity[1]; the flask is covered with a clock glass and placed in a boiling water-bath until the temperature of the solution is the same as that of the bath. The solution of the sample is then added and the mixture made up to 100 c.c. with boiling water, the flask then being covered with the clock glass and heated for exactly 12 minutes in the boiling water-bath. The precipitated cuprous oxide is filtered as quickly as possible in a Soxhlet tube or Gooch crucible, washed with hot water, then with a little alcohol and ether, dried and finally weighed after conversion to cupric oxide or metallic copper. This weight, multiplied by 500 gives the amount of cupric oxide or copper corresponding to 100 grms. of sample.

Another portion of the 10 per cent. solution of the sample is read in a 200 mm. tube in terms of Ventzke saccharimeter degrees.

A third portion (50 c.c.) of the 10 per cent. solution is used for determining the copper-reducing power and optical activity of the unfermentable matter (dextrin, etc.); for this the solution is sterilised by boiling for a few minutes, cooled, and fermented with 2 grms. of washed, pressed yeast at about 24° C. for about 48 hours or longer if necessary. The fermented solution is treated with a little alumina cream, made to 100 c.c. and filtered, the reducing power and Ventzke reading of the filtrate being determined.

The percentages of dextrose and maltose are now calculated as follows:—The difference between the weights of cupric oxide corresponding to 100 grms. of sample before and after fermentation represents the weight of oxide $a$, corresponding to the dextrose and maltose in 100 grms. of sample. The weight of oxide, $m$, corresponding to 1 grm. of dextrose and the weight of oxide, $p$, corresponding to 1 grm. of maltose are found from tables XII and XIII.

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[1] Cp. Davis and Daish, *J. Agric. Sci.*, 1913, **5**, 437.

Then if D is the percentage of dextrose and M that of maltose,

$$mD + pM = a \qquad (1)$$

Again, the Ventzke reading of the fermented solution (referred to the 10 per cent. solution of the original sample) is deducted from that of the 10 per cent. solution before fermentation, and the remainder, in Ventzke degrees, due to dextrose and maltose is converted into $[\alpha]_D$ by the equation:

## TABLE XII.

REDUCING POWER OF DEXTROSE UNDER BROWN, MORRIS AND MILLAR'S CONDITIONS.

| Sugar mgrms. | Cu grms. | CuO grms. | CuO corresponding to 1 grm. dextrose | Sugar mgrms. | Cu grms. | CuO grms. | CuO corresponding to 1 grm. dextrose |
|---|---|---|---|---|---|---|---|
| 50 | 0·1030 | 0·1289 | 2·578 | 130 | 0·2585 | 0·3241 | 2·493 |
| 55 | 0·1134 | 0·1422 | 2·585 | 135 | 0·2675 | 0·3354 | 2·484 |
| 60 | 0·1238 | 0·1552 | 2·587 | 140 | 0·2762 | 0·3463 | 2·473 |
| 65 | 0·1342 | 0·1682 | 2·589 | 145 | 0·2850 | 0·3573 | 2·464 |
| 70 | 0·1443 | 0·1809 | 2·585 | 150 | 0·2934 | 0·3673 | 2·448 |
| 75 | 0·1543 | 0·1935 | 2·580 | 155 | 0·3020 | 0·3787 | 2·443 |
| 80 | 0·1644 | 0·2061 | 2·577 | 160 | 0·3103 | 0·3891 | 2·432 |
| 85 | 0·1740 | 0·2187 | 2·572 | 165 | 0·3187 | 0·3996 | 2·422 |
| 90 | 0·1834 | 0·2299 | 2·555 | 170 | 0·3268 | 0·4098 | 2·410 |
| 95 | 0·1930 | 0·2420 | 2·547 | 175 | 0·3359 | 0·4200 | 2·400 |
| 100 | 0·2027 | 0·2538 | 2·538 | 180 | 0·3431 | 0·4302 | 2·390 |
| 105 | 0·2123 | 0·2662 | 2·535 | 185 | 0·3508 | 0·4399 | 2·377 |
| 110 | 0·2218 | 0·2781 | 2·528 | 190 | 0·3590 | 0·4501 | 2·369 |
| 115 | 0·2313 | 0·2900 | 2·522 | 195 | 0·3668 | 0·4599 | 2·358 |
| 120 | 0·2404 | 0·3014 | 2·512 | 200 | 0·3745 | 0·4689 | 2·344 |
| 125 | 0·2496 | 0·3130 | 2·504 | 205 | 0·3822 | 0·4792 | 2·338 |

$$[\alpha]_D = \frac{°V \times 10}{2} \times 0·346$$

Then, if this value of $[\alpha]_D$ is denoted by $b$,

$$52·7D + 138·0M = b \times 100 \qquad (2)$$

the values 52·7 and 138·0 being the specific rotations of dextrose and maltose. The values of D and M are found from equations (1) and (2). The method of calculation is illustrated as follows:

The 10 c.c. of the 2 per cent. solution used for copper reduction yielded 0·3305 grm. cupric oxide, whence 100 grms. sample would yield (0·3305 × 500) = 165·25 grms. cupric oxide. Again, after fermentation, 25 c.c. of the 5 per cent. solution of the sample reduced copper equivalent to 0·110 grm. cupric oxide; hence the unfermentable matter in 100 grms. sample would yield (0·110 × 80) = 8·80 grms. of cupric oxide, and the dextrose and maltose in 100 grms. of the sample would yield (165·25 — 8·80) = 156·45 grms. of cupric oxide.

## TABLE XIII.

### REDUCING POWER OF MALTOSE UNDER BROWN, MORRIS AND MILLAR'S CONDITIONS.

| Maltose mgrms. | Cu grms. | CuO grms. | CuO corresponding to 1 grm. maltose. | Maltose mgrms. | Cu grms. | CuO grms. | CuO corresponding to 1 grm maltose. |
|---|---|---|---|---|---|---|---|
| 70 | 0·0772 | 0·0966 | 1·380 | 190 | 0·2072 | 0·2593 | 1·371 |
| 75 | 0·0826 | 0·1034 | 1·380 | 195 | 0·2126 | 0·2661 | 1·370 |
| 80 | 0·0880 | 0·1102 | 1·379 | 200 | 0·2180 | 0·2729 | 1·370 |
| 85 | 0·0934 | 0·1169 | 1·379 | 205 | 0·2234 | 0·2797 | 1·370 |
| 90 | 0·0988 | 0·1237 | 1·378 | 210 | 0·2288 | 0·2865 | 1·369 |
| 95 | 0·1042 | 0·1305 | 1·378 | 215 | 0·2342 | 0·2933 | 1·369 |
| 100 | 0·1097 | 0·1373 | 1·378 | 220 | 0·2397 | 0·3000 | 1·3685 |
| 105 | 0·1151 | 0·1441 | 1·377 | 225 | 0·2451 | 0·3068 | 1·368 |
| 110 | 0·1205 | 0·1509 | 1·377 | 230 | 0·2505 | 0·3136 | 1·368 |
| 115 | 0·1259 | 0·1576 | 1·3765 | 235 | 0·2559 | 0·3203 | 1·367 |
| 120 | 0·1313 | 0·1644 | 1·376 | 240 | 0·2613 | 0·3272 | 1·367 |
| 125 | 0·1367 | 0·1712 | 1·376 | 245 | 0·2667 | 0·3340 | 1·3665 |
| 130 | 0·1422 | 0·1779 | 1·375 | 250 | 0·2722 | 0·3407 | 1·366 |
| 135 | 0·1476 | 0·1848 | 1·375 | 255 | 0·2776 | 0·3475 | 1·366 |
| 140 | 0·1530 | 0·1916 | 1·375 | 260 | 0·2830 | 0·3543 | 1·365 |
| 145 | 0·1584 | 0·1983 | 1·374 | 265 | 0·2884 | 0·3610 | 1·365 |
| 150 | 0·1634 | 0·2051 | 1·374 | 270 | 0·2938 | 0·3678 | 1·365 |
| 155 | 0·1692 | 0·2119 | 1·373 | 275 | 0·2992 | 0·3747 | 1·364 |
| 160 | 0·1747 | 0·2186 | 1·373 | 280 | 0·3047 | 0·3814 | 1·364 |
| 165 | 0·1801 | 0·2254 | 1·373 | 285 | 0·3101 | 0·3882 | 1·3635 |
| 170 | 0·1855 | 0·2323 | 1·372 | 290 | 0·3155 | 0·3950 | 1·363 |
| 175 | 0·1909 | 0·2390 | 1·372 | 295 | 0·3209 | 0·4017 | 1·363 |
| 180 | 0·1963 | 0·2458 | 1·3715 | 300 | 0·3264 | 0·4085 | 1·362 |
| 185 | 0·2017 | 0·2526 | 1·371 | 305 | 0·3318 | 0·4154 | 1·362 |

The polarimetric reading of the 10 per cent. solution of the sample in a 200 mm. tube was 26·1° V. and that of the 5 per cent. solution after fermentation was 0·75° V., hence the Ventzke reading due to dextrose and maltose was

$$\{26{\cdot}1 - (0{\cdot}75 \times 2)\} = 24{\cdot}6$$

and

$$[\alpha]_D = \left(\frac{24{\cdot}6 \times 10 \times 0{\cdot}346}{2}\right) = 42{\cdot}56.$$

From Tables XII and XIII it is found that with copper reduction equivalent to 0·3305 grm. of cupric oxide the grm. value for dextrose is 2·488 and that for maltose is 1·367. Substituting these data in equations (1) and (2) we have:—

$$2{\cdot}488D + 1{\cdot}367M = 156{\cdot}45$$
$$52{\cdot}7D + 138M = 42{\cdot}56 \times 100$$

Whence: percentage of dextrose in sample = 58·1
percentage of maltose in sample = 8·6.

The above scheme of analysis may be modified by replacing the gravimetric method of copper reduction by Lane and Eynon's[1] volumetric method with methylene blue as internal indicator; the method is both accurate and expeditious:—

The Fehling's solution used is that known as Soxhlet's modification and is prepared by mixing equal volumes of solutions (A) and (B):—

(A) 34·639 grms. of pure crystallised copper sulphate[2] $CuSO_4.5H_2O$ are dissolved in distilled water and made up to 500 c.c.

(B) 173 grms. of Rochelle salt and 50 grms. of sodium hydroxide are dissolved in distilled water and made up to 500 c.c.

The methylene blue indicator is prepared by dissolving 1 grm. of methylene blue in water and making up to 100 c.c.; this solution will keep unchanged indefinitely.

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[1] *J. Soc. Chem. Ind.*, 1923, **42**, 32T.

[2] The preparation of pure crystallised copper sulphate, exactly corresponding to the formula $CuSO_4, 5H_2O$, is both troublesome and tedious (cp. Lane and Eynon, *J. Soc. Chem. Ind.*, 1925, **44**, 150T.) It is preferable to standardise the Fehling's solution with pure invert sugar, dextrose or maltose and adjust its concentration to accord with the tables given in conjunction with the method.

It is advisable, in order to insure the greatest accuracy, to make two titrations, the first by what is called the "incremental method," to ascertain approximately the volume of sugar solution required, and the second by what is called the "standard method," in which almost the whole of the sugar solution required to effect reduction is added in the first instance.

The sample of starch sugar or syrup should be made up to a solution of 0·2 to 1·0 per cent. concentration.

*Incremental Method of Titration.*—10 or 25 c.c. of Fehling's solution, in a 300–400 c.c. flask, is treated cold with 15 c.c. of the sugar solution, and without further dilution heated to boiling over a wire gauze. After the liquid has been boiling for about 15 seconds it will be possible to judge if the copper is almost all reduced, by the bright red colour imparted to the boiling liquid by the suspended cuprous oxide. If it is judged that nearly all the copper is reduced, a few drops of the methylene blue indicator are added, boiling is continued for 1–2 minutes from the commencement of ebullition, and then the sugar solution is added in small quantities, say 1 c.c. or less at a time, the liquid being allowed to boil for about 10 seconds between successive additions, until the colour of the indicator is completely discharged. If after the mixture of Fehling's solution with 15 c.c. of sugar solution has been boiling for about a quarter of a minute there appears to be still much unreduced copper, a further 10 c.c. of sugar solution is added and the whole allowed to boil for a quarter of a minute, and so on until it is considered unsafe to add a further large increment of sugar solution; boiling is then continued for 1–2 minutes, after which the indicator is added and the titration is completed by small additions of the sugar solution. It is advisable not to add the indicator until the neighbourhood of the end-point has been reached, for the same reason that in the titration of iodine with thiosulphate solution the addition of starch indicator is best postponed to as late a stage as possible, viz., because the indicator retains its full colour until the end-point is almost reached and thus gives no warning to the operator to go slowly.

When the operator has had a fair amount of experience with the method a sufficiently accurate result may often be obtained by a single estimation by the incremental method, but for the utmost degree of accuracy of which the method is capable a second titration should be made by the standard method of titration.

*Standard Method of Titration.*—10 to 25 c.c. of Fehling's solution is measured into a flask of 300 to 400 c.c. capacity, and treated cold with almost the whole of the sugar solution required to effect reduction of all the copper, so that if possible not more than 1 c.c. is required later to complete the titration. The flask containing the cold mixture is heated over a wire gauze; after the liquid has begun to boil it is kept in moderate ebullition for 2 minutes, and then, without removal of the flame, 3–5 drops of the methylene blue indicator are added, and the titration is completed in 1 minute further, so that the reaction liquid boils altogether for 3 minutes without interruption.

The indicator is so sensitive that the end-point can be determined to within one drop of the sugar solution in many cases. The complete decolorisation of the methylene blue is usually sufficiently well indicated by the whole reaction liquid, in which the cuprous oxide is continuously churned up, becoming bright red or orange in colour; but in case of doubt the flask may be removed from the wire gauze for a second or two (a holder of folded paper is very convenient for this purpose as it can be left round the neck of the flask without risk of overbalancing), and held against a sheet of white paper on the bench, when the edge of the liquid will appear bluish if the indicator is not completely decolorised. It is inadvisable to interrupt the boiling for more than a few seconds, as the indicator undergoes back-oxidation rather rapidly when air is allowed free access into the flask, but there is no danger of this so long as a continuous stream of steam is issuing from the mouth of the flask.

It should be observed that with both incremental and standards methods, the flask containing the reaction mixture is left on the wire gauze over the Bunsen flame throughout the whole titration, except when it may be removed for a

# TABLE XIV.

## DEXTROSE TABLE.

(All figures relate to anhydrous dextrose $C_6H_{12}O_6$.)

| C.c. of sugar solution required | For 10 c.c. of Fehling's solution. | | | For 25 c.c. of Fehling's solution. | | |
|---|---|---|---|---|---|---|
| | Dextrose factor.* | Mgrms. of dextrose per 100 c.c. | C.c. of Fehling's solution corres-ponding to 1 grm. of dextrose. | Dextrose factor.† | Mgrms. of dextrose per 100 c.c. | C.c. of Fehling's solution corres-ponding to 1 grm. of dextrose. |
| 15 | 49·1 | 327 | 203·6 | 120·2 | 801 | 208·0 |
| 16 | 49·2 | 307 | 203·1 | 120·2 | 751 | 208·0 |
| 17 | 49·3 | 289 | 202·7 | 120·2 | 707 | 207·9 |
| 18 | 49·3 | 274 | 202·3 | 120·2 | 668 | 207·8 |
| 19 | 49·4 | 260 | 202·0 | 120·3 | 633 | 207·7 |
| 20 | 49·5 | 247·4 | 201·8 | 120·3 | 601·5 | 207·7 |
| 21 | 49·5 | 235·8 | 201·6 | 120·3 | 572·9 | 207·6 |
| 22 | 49·6 | 225·5 | 201·4 | 120·4 | 547·3 | 207·5 |
| 23 | 49·7 | 216·1 | 201·2 | 120·4 | 523·6 | 207·4 |
| 24 | 49·8 | 207·4 | 200·9 | 120·5 | 501·9 | 207·4 |
| 25 | 49·8 | 199·3 | 200·7 | 120·5 | 482·0 | 207·3 |
| 26 | 49·9 | 191·8 | 200·5 | 120·6 | 463·7 | 207·2 |
| 27 | 49·9 | 184·9 | 200·3 | 120·6 | 446·8 | 207·2 |
| 28 | 50·0 | 178·5 | 200·1 | 120·7 | 431·1 | 207·1 |
| 29 | 50·0 | 172·5 | 199·9 | 120·7 | 416·4 | 207·0 |
| 30 | 50·1 | 167·0 | 199·6 | 120·8 | 402·7 | 207·0 |
| 31 | 50·2 | 161·8 | 199·4 | 120·8 | 389·7 | 206·9 |
| 32 | 50·2 | 156·9 | 199·2 | 120·8 | 377·6 | 206·8 |
| 33 | 50·3 | 152·4 | 199·0 | 120·9 | 366·3 | 206·8 |
| 34 | 50·3 | 148·0 | 198·7 | 120·9 | 355·6 | 206·7 |
| 35 | 50·4 | 143·9 | 198·5 | 121·0 | 345·6 | 206·6 |
| 36 | 50·4 | 140·0 | 198·3 | 121·0 | 336·3 | 206·5 |
| 37 | 50·5 | 136·4 | 198·1 | 121·1 | 327·4 | 206·5 |
| 38 | 50·5 | 132·9 | 197·9 | 121·2 | 318·8 | 206·4 |
| 39 | 50·6 | 129·6 | 197·7 | 121·2 | 310·7 | 206·3 |
| 40 | 50·6 | 126·5 | 197·5 | 121·2 | 303·1 | 206·2 |
| 41 | 50·7 | 123·6 | 197·3 | 121·3 | 295·9 | 206·1 |
| 42 | 50·7 | 120·8 | 197·1 | 121·4 | 289·0 | 206·0 |
| 43 | 50·8 | 118·1 | 196·9 | 121·4 | 282·4 | 205·9 |
| 44 | 50·8 | 115·5 | 196·7 | 121·5 | 276·1 | 205·8 |
| 45 | 50·9 | 113·0 | 196·5 | 121·5 | 270·1 | 205·7 |
| 46 | 50·9 | 110·6 | 196·4 | 121·6 | 264.3 | 205·6 |
| 47 | 51·0 | 108·4 | 196·2 | 121·6 | 258·8 | 205·5 |
| 48 | 51·0 | 106·2 | 196·0 | 121·7 | 253·5 | 205·4 |
| 49 | 51·0 | 104·1 | 195·8 | 121·7 | 248·4 | 205·3 |
| 50 | 51·1 | 102·2 | 195·7 | 121·8 | 243·6 | 205·3 |

* Mgrms. of dextrose corresponding to 10 c.c. of Fehling's solution.
† Mgrms. of dextrose corresponding to 25 c.c. of Fehling's solution.

## TABLE XV.

### MALTOSE TABLE.

(All figures relate to anhydrous maltose $C_{12}H_{22}O_{11}$.)

| C.c. of sugar solution required | For 10 c.c. of Fehling's solution. | | | For 25 c.c. of Fehling's solution. | | |
|---|---|---|---|---|---|---|
| | Maltose factor.* | Mgrms. of maltose per 100 c.c. | C.c. of Fehling's solution corresponding to 1 grm. of maltose. | Maltose factor.† | Mgrms. of maltose per 100 c.c. | C.c. of Fehling's solution corresponding to 1 grm. of maltose. |
| 15 | 77·2 | 515 | 129·5 | 197·8 | 1319 | 126·4 |
| 16 | 77·1 | 482 | 129·7 | 197·4 | 1233 | 126·7 |
| 17 | 77·0 | 453 | 129·8 | 197·0 | 1159 | 126·9 |
| 18 | 77·0 | 427 | 130·0 | 196·7 | 1093 | 127·1 |
| 19 | 76·9 | 405 | 130·1 | 196·5 | 1034 | 127·3 |
| 20 | 76·8 | 383·8 | 130·3 | 196·2 | 980·7 | 127·5 |
| 21 | 76·7 | 365·1 | 130·4 | 195·8 | 932·5 | 127·7 |
| 22 | 76·6 | 348·1 | 130·6 | 195·5 | 888·7 | 127·9 |
| 23 | 76·5 | 332·5 | 130·7 | 195·1 | 848·5 | 128·1 |
| 24 | 76·4 | 318·3 | 130·9 | 194·8 | 811·8 | 128·3 |
| 25 | 76·4 | 305·4 | 131·0 | 194·5 | 778·1 | 128·5 |
| 26 | 76·3 | 293·4 | 131·2 | 194·2 | 747·0 | 128·7 |
| 27 | 76·2 | 282·2 | 131·3 | 193·9 | 718·2 | 128·9 |
| 28 | 76·1 | 271·8 | 131·4 | 193·6 | 691·5 | 129·1 |
| 29 | 76·0 | 262·2 | 131·5 | 193·3 | 666·6 | 129·3 |
| 30 | 76·0 | 253·3 | 131·6 | 193·0 | 643·4 | 129·5 |
| 31 | 75·9 | 244·9 | 131·7 | 192·8 | 621·6 | 129·7 |
| 32 | 75·9 | 237·2 | 131·8 | 192·5 | 601·4 | 129·9 |
| 33 | 75·8 | 229·8 | 131·9 | 192·2 | 582·4 | 130·1 |
| 34 | 75·8 | 222·9 | 132·0 | 191·9 | 564·6 | 130·3 |
| 35 | 75·7 | 216·2 | 132·1 | 191·7 | 547·7 | 130·5 |
| 36 | 75·6 | 210·0 | 132·2 | 191·4 | 531·7 | 130·6 |
| 37 | 75·6 | 204·3 | 132·3 | 191·2 | 516·7 | 130·8 |
| 38 | 75·5 | 198·7 | 132·4 | 191·0 | 502·5 | 131·0 |
| 39 | 75·5 | 193·6 | 132·5 | 190·8 | 489·0 | 131·1 |
| 40 | 75·4 | 188·6 | 132·6 | 190·5 | 476·2 | 131·2 |
| 41 | 75·4 | 184·3 | 132·6 | 190·3 | 464·1 | 131·4 |
| 42 | 75·3 | 179·4 | 132·7 | 190·1 | 452·5 | 131·5 |
| 43 | 75·3 | 175·1 | 132·8 | 189·8 | 441·5 | 131·7 |
| 44 | 75·2 | 171·0 | 132·9 | 189·6 | 430·9 | 131·8 |
| 45 | 75·2 | 167·1 | 132·9 | 189·4 | 420·9 | 131·9 |
| 46 | 75·1 | 163·4 | 133·0 | 189·2 | 411·4 | 132·1 |
| 47 | 75·1 | 159·9 | 133·1 | 189·0 | 402·4 | 132·2 |
| 48 | 75·1 | 156·5 | 133·2 | 188·9 | 393·7 | 132·3 |
| 49 | 75·0 | 153·1 | 133·3 | 188·8 | 385·2 | 132·4 |
| 50 | 75·0 | 150·1 | 133.3 | 188·7 | 377·3 | 132·5 |

* Mgrms. of maltose corresponding to 10 c.c. of Fehling's sloution.

† Mgrms. of matlose corresponding to 25 c.c. of Fehling's solution.

few seconds to ascertain if the end-point is reached. In adding sugar solution to the reaction mixture the burette may be held in the hand over the flask. The burette may be fitted with a small outlet tube bent twice at right angles, so that the body of the burette can be kept out of the steam while the jet is held over the mouth of the flask. Burettes with glass taps are unsuitable for this work, as the taps become heated by the steam and are very liable to jam.

Tables XIV and XV show, for the standard method of titration, the values corresponding to integral cubic centimetres of the sugar solutions, intermediate figures being obtained by interpolation.

In calculating the percentages of dextrose and maltose from the difference between reducing powers before and after fermentation as determined by Lane and Eynon's procedure described above, and the difference between the polarisations before and after fermentation, the forms of the equations (1) and (2) previously given (see p. 237) are used save that in equation (1) $a$ represents the number of c.c. of Fehling's solution reduced by the dextrose and maltose in 100 grms. of the sample, and $m$ and $p$ represent the numbers of c.c. of Fehling's solution corresponding to 1 grm. of dextrose and maltose respectively.

The percentage of unfermentable matter in starch sugar is found by deducting the sum of the percentages of dextrose, maltose, ash, protein and water from 100.

# LIST OF ABBREVIATIONS USED IN THE REFERENCES.

| | |
|---|---|
| *Amer. Chem. J.* | *American Chemical Journal.* |
| *Amer. J. Pharm.* | *American Journal of Pharmacy.* |
| *Amer. J. Sci.* | *American Journal of Science.* |
| *Annalen* | *Liebig's Annalen der Chemie.* |
| *Ann. Brass. et Dist.* | *Annales de la Brasserie et de la Distillerie.* |
| *Ann. Chim. anal.* | *Annales de Chimie analytique.* |
| *Ann. Chim. Phys.* | *Annales de Chimie et de Physique.* |
| *Ann. Bot.* | *Annals of Botany.* |
| *Arkiv. Kem. Min. Geol.* | *Arkiv. för Kemi, Mineralogi och Geologi.* |
| *Baeyerisches Brauer J.* | *Baeyerisches Brauerjournal.* |
| *Ber. Deut. bot. Ges.* | *Berichte der Deutschen botanischen Gesellschaft.* |
| *Ber.* | *Berichte der Deutschen chemischen Gesellschaft.* |
| *Ber. Deut. pharm. Ges.* | *Berichte der Deutschen pharmazeutischen Gesellschaft.* |
| *Biochem. J.* | *Biochemical Journal.* |
| *Biochem. Zeitsch.* | *Biochemische Zeitschrift.* |
| *Bot. Zeit.* | *Botanische Zeitung.* |
| *Bull. Imp. Inst.* | *Bulletin of the Imperial Institute.* |
| *Bull. Pharm.* | *Bulletin de Pharmacie.* |
| *Bull. Soc. chim.* | *Bulletin de la Société chimique de France.* |
| *Bull. Soc. chim. Belg.* | *Bulletin de la Société chimique de Belgique.* |
| *Bull. Soc. Ind. Mulhouse* | *Bulletin de la Société Industrielle de Mulhouse.* |
| *Cereal Chem.* | *Cereal Chemistry.* |
| *Chem. News* | *Chemical News.* |
| *Chem. Soc. Trans.* | *Chemical Society Transactions.* |
| *Chem. Weekblad* | *Chemisch Weekblad.* |
| *Chem. Zeit.* | *Chemiker-Zeitung.* |

| | |
|---|---|
| *Chem. Zentr.* | *Chemisches Zentralblatt.* |
| *Compt. rend.* | *Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.* |
| *Ding. Polyt. J.* | *Dingler's Polytechnische Journal.* |
| E.P. | English Patent. |
| F.P. | French Patent. |
| G.P. | German Patent. |
| *Guinness Research Lab. Trans.* | *Guinness Research Laboratory Transactions.* |
| *Helv. Chim. Acta* | *Helvetica Chimica Acta.* |
| *Int. Congr. Appl. Chem.* | *International Congress of Applied Chemistry.* |
| *J. Agric. Sci.* | *Journal of Agricultural Science.* |
| *J. Amer. Chem. Soc.* | *Journal of the American Chemical Society.* |
| *J. Ind. Eng. Chem.* | *Journal of Industrial and Engineering Chemistry.* |
| *J. Inst. Brew.* | *Journal of the Institute of Brewing.* |
| *J. Physical Chem.* | *Journal of Physical Chemistry.* |
| *J. pr. Chem.* | *Journal für praktische Chemie.* |
| *J. Russ. Phys. Chem. Soc.* | *Journal of the Physical and Chemical Society of Russia.* |
| *J. Soc. Chem. Ind.* | *Journal of the Society of Chemical Industry.* |
| *J. Soc. Dyers and Col.* | *Journal of the Society of Dyers and Colourists.* |
| *J. Text. Inst.* | *Journal of the Textile Institute.* |
| *Koll. Chem. Beihefte* | *Kolloidchemische Beihefte.* |
| *Monatsh.* | *Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.* |
| *Monit. Scient.* | *Moniteur Scientifique.* |
| *Neue Zeitsch. Rüb-Zuck. Ind.* | *Neue Zeitschrift für Rübenzucker Industrie.* |
| *Österr. bot. Zeitsch.* | *Österreichische botanische Zeitschrift.* |
| *Papier Zeit.* | *Papier Zeitung.* |
| *Pflüger's Archiv.* | *Archiv für die gesamte Physiologie des Menschen und der Thiere.* |
| *Pharm. J.* | *Pharmaceutical Journal.* |
| *Proc. Brit. Assoc.* | *Proceedings of the British Association.* |
| *Proc. Phys. Soc. London* | *Proceedings of the Physical Society of London.* |

| | |
|---|---|
| *Proc. Roy. Soc.* .. .. | *Proceedings of the Royal Society.* |
| *Schweigg. J.* .. .. | *Schweigger's Journal.* |
| U.S.P. .. .. .. | United States Patent |
| *Woch. f. Brau.* .. .. | *Wochenschrift für Brauerei.* |
| *Wochenbl. Papierfabr.* .. | *Wochenblatt für Papierfabrikation.* |
| *Zeitsch. anal. Chem.* .. | *Zeitschrift für analytische Chemie.* |
| *Zeitsch. angew. Chem.* .. | *Zeitschrift für angewandte Chemie.* |
| *Zeitsch. anorg. Chem.* .. | *Zeitschrift für anorganische und allgemeine Chemie.* |
| *Zeitsch. Deut. Ver. Rübenzucker.* .. .. | *Zeitschrift des Vereins die Rübenzucker-Industrie des Deutschen Reichs.* |
| *Zeitsch. ges. Brauw.* .. | *Zeitschrift für das gesamte Brauwesen.* |
| *Zeitsch. öffentl. Chem.* .. | *Zeitschrift für öffentliche Chemie.* |
| *Zeitsch. Nahr.-Genussm.* . | *Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.* |
| *Zeitsch. Spiritusind.* .. | *Zeitschrift für Spiritusindustrie.* |
| *Zentr. Bakt. u. Parasitenk.* | *Zentralblatt für Bakteriologie und Parasitenkunde.* |

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