

and the humidity lowered to a degree sufficient to inactivate the bulk of the enzymes and the leaf is killed. Finally the temperature is raised high enough to completely dry out the midrib of the leaf as well as the leaf blade. The leaf is now very brittle, and before being handled it must be permitted to absorb moisture. When this has been completed, the leaf is placed in stacks called "bulks." Here the leaf is left until graded. During this waiting time further changes take place in which an improvement in colour occurs and it is possible also that the small amount of enzyme left after curing carries on its work of hydrolysis slowly. After grading, the leaf passes to the manufacturer, who usually holds the leaf for several years. During this time the tobacco becomes more mellow, this being accompanied by a reduction in the nicotine and tannin contents and a conversion of proteins into amides. Some of the fats, gums and resins are also broken down.

Chemical Criteria of Quality.—Quality in tobacco cannot be ascribed wholly to any one constituent or group of constituents; both the inorganic and organic compounds exert an influence.

(a) *Inorganic Constituents.*—Tobacco leaf commonly contains from 10 to 25 per cent of ash, of which the bulk is made up of lime and potash as carbonates derived from the decomposition of the corresponding salts of organic acids. For good cigarette leaf the lower figure should be aimed at. A certain amount of lime is required, otherwise a white ash will not be obtained on smoking the tobacco. Too little or too much magnesia tends to produce a tobacco of unsatisfactory burning quality; if too little, then a black ash is obtained; if too much, the fireholding capacity is injured. The potash content has an important effect on the burning quality of the leaf. Claims have been made that at least 5 per cent of K_2O should be present in the dry matter of the leaf, but this appears to be higher than is attained in this country. New Zealand leaf examined to date has shown in the light cigarette types only about 2 per cent. Some of the imported American tobacco shows a higher potash content but has not approached the 5 per cent looked for by some European authorities. It is also important that a large proportion of the potash should be present in combination with organic acids such as malic, citric and oxalic. Phosphoric acid (P_2O_5) content does not seem to have any important effect on burning quality. Chlorine on the other hand, if present to the extent of more than about 0.5 per cent, affects detrimentally the burning qualities. Inorganic sulphur content should also be low. An idea of the

type of analytical figures found for tobacco leaf used in New Zealand may be obtained from the following data; the figure for New Zealand leaf is an average one for a number of samples of leaf suitable for cigarettes; the United States of America figure is an average of two samples of leaf imported for blending purposes.

Percentages expressed on dry matter basis:

Origin	Total Soluble		CaO.	MgO.	P_2O_5	K_2O
	Ash	Ash				
New Zealand	12.87	11.99	4.33	0.89	0.51	1.98
U.S.A.	9.94	8.88	2.50	0.47	0.54	2.31
Standard (U.S.A.)	10	—	3.5	1.0	0.4-1.0	2.5-3.5

The main distinctions between the two sets of data are in the ash and lime contents. From the standard figures it would appear that the New Zealand leaf tends to be low in potash and high in total ash. Individual samples have been found to vary widely from the suggested data.

(b) *Organic Constituents.*—Tobacco leaf, in common with other plant materials, is composed of protein, carbohydrates and acids with a small amount of fats, resins and ethereal oils. In view of the larger number of constituents, a considerable change in any one of them may require to occur before an appreciable effect can be detected in the quality of the leaf. Influences favourable to quality are exerted by high contents of reducing sugars, dextrans and starch, while gums and resins tend to improve aroma. Investigations in New Zealand show that the best quality leaves are high in reducing sugars, the figure varying from 21 to 27 per cent calculated as glucose. Other related compounds such as pectins, pentosans, lignin and cellulose are reported to decrease as the quality of the leaf improves. Of the nitrogen compounds protein increases as the quality falls. Amide nitrogen content, which is a sign of well-cured and fermented leaf, increases with the improvement in quality, but the reverse is true for the percentage of nitrogen in the ammonia form. Nicotine content is usually relatively low, at one or two per cent, in good cigarette tobacco, but there is no strict relationship between total nicotine content and quality; rather does it appear that the amount of "free" nicotine decides to some extent the strength of the tobacco. For New Zealand tobaccos a range of nitrogen content from 1.6 to 3.2 per cent has been found for the same variety, the highest figures being found with the poorer quality leaf. Some samples of good imported American tobacco showed from 1.5 to 2.4 per cent. The best correlation with quality in a series

of 23 samples of New Zealand tobaccos was found in the value of the ratio total reducing sugars to total nitrogen. This ranged from 12.7 to 16.6 in the best leaf, down to as low as 2.7 to 7.7 for fair quality leaf. Further work is required however, before definite standards can be set from such data.

In a number of countries tobacco research is being actively prosecuted, but mostly the correlation between quality and analytical figures are given for a particular constituent such as potash or magnesium. In Australia however, the work has proceeded in the direction of seeking for an analytical reaction which will deal with a group of compounds; for example "lead number," "picric acid number" and "methylene-blue number" to represent compounds precipitable by lead acetate or picric acid, or reacting with methylene blue are found to correlate to some extent with quality, low lead number and low picric acid number, but high methylene blue number (and high reducing sugar content) go with good quality. To date the tendency in New Zealand has been to concentrate on determinations of particular constituents and build up a body of information for both organic and inorganic constituents on tobacco of known history and grading, which can later be examined for possible correlation of a constituent or group of constituents with quality. At the present time a sufficient body of such information has not been built up, and in view of the varying standards of tobacco in different countries it does not appear wise to place too much confidence in overseas results as a means of interpreting results obtained on New Zealand leaf.

Nicotine.—Nicotine is the distinctive alkaloid of tobacco. It is present in all tobacco in amounts varying from less than 1 per cent to more than 10 per cent according to the variety, strain and conditions of growth. For tobaccos used for smoking, the nicotine content ranges between about 1 and 3 per cent. New Zealand tobacco contains about 2 per cent of nicotine.

"Strength" of tobacco is not a direct function of its nicotine content; indeed total nicotine content does not appear to be correlated with quality. A high proportion of "free" nicotine, that is nicotine not combined with acids, however, appears to detrimentally affect quality. For New Zealand tobaccos examined to date the pH value of aqueous suspensions is so low that practically none of the nicotine is "free."

During the grading and manufacture of tobacco, a large amount of broken leaf, midribs, etc., become waste and is normally destroyed. From this waste a very useful amount

of nicotine could be obtained for use in the stock and horticultural industries. Work is being done in New Zealand and Australia on problems connected with the recovery of nicotine from such waste. A considerable amount of basic work has had to be done owing to the dearth of information in the literature and to the fact that most of the commercial processes are regarded as secret by the nicotine manufacturers. The process it is proposed to use here depends on the extraction of the nicotine from the tobacco waste by hydrocarbon solvents followed by the removal of the nicotine from the hydrocarbon by acid solutions. It is believed that a satisfactory process has been developed.

Tobacco Mosaic.—No account of tobacco chemistry would be complete without mention of "mosiac," a virus disease of tobacco. If the plant is severely affected in the young stage, stunting of the plant occurs; badly affected leaves are also of poor quality. Mosaic also decreases the nicotine content, but the chief interest of mosaic to the chemist lies in the fact that with development of symptoms in susceptible plants a considerable development of protein occurs. This protein, or a product from it, has been isolated in a crystalline form. Inoculation of plants with this substance causes development of symptoms of the disease. The crystalline material appears to be a nucleo-protein, of which the nucleic acid is very similar to nucleic acid from yeast. No new amino-acids have been obtained from the substance on hydrolysis. A wide field of work is opened up to the chemist in the investigation of this disease.

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CHEMISTRY IN THE FERTILISER INDUSTRY.

F. H. V. FIELDER

The use of fertilisers is probably as old as agriculture itself, but the chemical fertiliser industry, as we know it today dates from the commencement of the manufacture of superphosphate. This industry, with its concomitant industry—the manufacture of sulphuric acid—is today New Zealand's largest chemical industry and it is somewhat of a coincidence that the centennial of New Zealand should also mark the completion of one hundred years since the first publication of the suggestion for treating bones with sulphuric acid in order to render the phosphate in them more readily available to plants. This suggestion was made by the German chemist Liebig in 1840, but the real credit for the establishment of the superphosphate industry must be given to J. B. Lawes who, in 1842, was granted a patent covering the treatment of such substances as apatite and phosphorite with acid so as to make the phosphate in them soluble in water. Lawes had however, experimented with the idea for several years and had in 1840, used superphosphate on turnips at Rothamsted. From this beginning the superphosphate industry has expanded until the present world production exceeds 15,000,000 tons per annum.

A period of over forty years was to elapse before the manufacture of superphosphate was commenced in New Zealand. It is interesting to recall that in 1881 the government offered a bonus of £500 per annum for three years for the production each year of not less than fifty tons of sulphuric acid of good marketable quality. With characteristic enterprise the late Mr. T. W. Kempthorne, founder of the firm of Kempthorne Prosser & Co.'s N.Z. Drug Co. Ltd., erected a small acid unit at Burnside, near Dunedin and secured payment of the bonus to his company. In the subsequent three or four years the plant was extended and the manufacture of superphosphate commenced. A few years later operations were extended to Westfield, near Auckland, but after this little progress appears to have been made until about twenty years ago. During the last two decades the manufacture of superphosphate has been increased very greatly and is now carried on by four companies operating a total of eight up-to-date plants, situated near Auckland(3); New Plymouth(1); Wanganui(1); Christchurch(1); Dunedin(2). The extent of the industry is shown by the fact that the tonnage of superphosphate produced annually now exceeds 400,000 tons, valued at about £1,500,000.

The raw materials used in the industry are not found locally and are imported from overseas. For the manufacture of sulphuric acid, sulphur and nitrate of soda are required, the former being obtained from Texas (U.S.A.) and Japan, and the latter from Chile. The rock phosphate, which is treated with sulphuric acid is obtained from Nauru and Ocean Islands and is of the highest grade. The administration of these islands is in the hands of the British Phosphate Commission which has installed extensive equipment for mining, drying and loading the phosphate.

Briefly, the manufacture of superphosphate is as follows: The raw rock phosphate is first ground to powder and then mixed intimately with the requisite quantity of sulphuric acid, either batch or continuous types of mixers being employed. The mixture, which becomes hot from the heat of the chemical reaction and has the consistency of porridge, is run into an enclosed receptacle situated beneath the mixer and called a "den." Successive mixes are run in until the den is full and in about half an hour the whole has set into a soft but solid mass. The den is then opened and the contents removed by means of a mechanical excavator and conveyed by mechanical means to a storage shed where it is allowed to mature. It has then only to be screened and bagged.

Superphosphate forms the basis of the great majority of all fertilisers sold in this country. Basic and ammoniated superphosphates are made by adding lime and sulphate of ammonia respectively to the hot superphosphate as it emerges from the den. Mixed fertilisers are compounded with superphosphate as the main ingredient with the addition of potash and various forms of nitrogen. There are no known potash deposits in New Zealand so the whole of this material has to be imported. Formerly the greater part of the nitrogen was supplied by means of bonedust, blood and bone, or dried blood, which were in plentiful supply as by-products of the meat freezing industry. In recent years improved methods adopted in this industry have greatly reduced the amount of material which could be sold only for fertiliser purposes and consequently greater and greater use has been made of imported sulphate of ammonia. Sulphate of ammonia is made by "fixation" of the nitrogen of the air. The plant required however, is costly to instal and is economical only in large capacity units. The nitrogen requirements of this country are relatively small and up to the present are insufficient to justify the erection of a plant here. A plant is at present in course of erection in Australia. Of other imported fertilisers, Basic Slag, a by-product of the steel industry, is the most important. Soft

phosphate rock, a product of Northern Africa and various guanos are the only others used in important quantities.

An important development in agriculture during the last few years is the recognition of the importance in both the animal and vegetable organism of the so called minor elements. Formerly the only mineral elements thought to be essential for their growth were those found in quantity in the ashes of plants, such as calcium, potassium, sodium, iron, aluminium, silicon, magnesium, sulphur and phosphorus. The older methods of analysis were not sufficiently refined to detect and estimate the very small quantities of the other elements. By the use of the spectroscope and other modern methods the presence of fifty or sixty elements has been shown in the animal and vegetable organism, but it still remains to be proved that all of these are essential. Several diseases of both plants and animals have been shown to be due to deficiency of one or more of these minor elements. The most striking examples in this country are those of boron and cobalt. A deficiency of boron has been shown to be the cause of such diseases as brown heart in turnips and internal cork in apples. The addition of borax to suitable fertiliser mixtures enables these diseases to be controlled.

In several districts in New Zealand, but notably in the central portions of the North Island where the soil is derived from volcanic ash, there exists a wasting disease of ruminant animals characterised by excessive anaemia and commonly called "Bush Sickness." After many years of investigation and research it has been shown that the disease is caused by a deficiency of the comparatively rare element, cobalt. A specially prepared cobaltised superphosphate is now made and is finding increasing use in districts affected with bush sickness. In other countries deficiency diseases due to a deficiency of manganese, copper and zinc have been reported. Although in this country no diseases have been definitely traced to a deficiency of these three elements, fertilisers containing small quantities of them are on the market. Possibly the beneficial effects of basic slag on some soils is due to one or more of the minor elements it contains.

As mentioned previously the manufacture of sulphuric acid is an essential part of the fertiliser industry and as this is a somewhat complicated process requiring constant chemical control, the industry has, from its inception, given employment to chemists. In addition to exercising technical control over the sulphuric acid plant, the successful production of a superphosphate of maximum solubility and of good physical

condition requires constant supervision by means of chemical analysis of the raw materials and at various stages in the course of manufacture. In accordance with the requirements of the Fertilisers Act, the analysis of all fertilisers must be guaranteed and the chemist must constantly check the analysis of outgoing fertilisers to see that they are up to guarantee. These and other routine matters keep the fertiliser chemist too busy to allow of his engaging in the original investigations necessary to solve such a problem as the cause of a deficiency disease. Problems such as this, are best left to the research laboratories of the Department of Agriculture and to research institutions such as the Cawthron Institute. After the researches of these institutions have established that a fertiliser containing a particular element in small quantity is necessary to combat the trouble, it remains for the fertiliser chemist to devise ways and means for manufacturing the desired material on a large scale and to see that the finished product conforms to the requirements established by research.

From this short review of the fertiliser industry it will be seen that chemistry and the chemist have played an all important part in its progress. As the functions of the minor elements in biochemical processes become better understood, the chemistry of fertilisers will become more and more complex and the necessity for chemical control greater than ever, and to the problem of making two blades of grass grow where but one grew before is added the problem of making sure that those two blades contain all the essential elements in proper proportion and possess the utmost nutritive and health sustaining qualities.

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FOOD AND DRUGS—THEIR ADULTERATION

R. L. ANDREW

This paper gives a sketch of the role of the chemist in the administration of the Sale of Food and Drugs Act of New Zealand.

In the early days of the country some action was taken to prevent the sale of adulterated foods, particular attention being paid to milk and alcoholic liquors, but no really effective action was possible until the Sale of Food and Drugs Act, 1908 became law. This Act is modelled on the corresponding English Act, but its administration is different as proceedings are taken usually for failing to comply with standards laid down in Regulations under the Act. In English practice, with some exceptions, the standards are decided by the courts after hearing evidence. The regulations can be regarded as a comprehensive set of standards with which foods must comply. They were first issued in 1913 and have since, as appeared desirable, been subjected to additions and amendments. Drugs sold must comply with the standards of the British Pharmacopoeia or British Pharmaceutical Codex and in a few cases with special standards. The Sale of Food and Drugs Act is administered by the Department of Health and in this paper only the analyst's part in this administration will be dealt with.

Analysts appointed specially for the purposes of the Act are stationed at each of the four main centres. They are Government chemists on the staff of the Dominion Laboratory. The enforcement of the Act, which depends mainly on the findings of the analyst, has had spectacular results in the last thirty years. Many instances of what were everyday types of adulteration have ceased to be, pepper is no longer mixed with ground rice, jams are true to label, baking powders are full strength and so on.

I have space to deal with only one foodstuff in particular, and that is milk, as it is the most important of foods and illustrates what can be done by the use of improved methods of analysis. In 1908, the only practicable examination of milk was for fat, solids not fat, and preservatives. The presence of added water could not be proved and there were no practicable tests for ascertaining the bacteriological quality of milk or whether it had been properly pasteurised.

The first great advance was the adoption of the freezing point test for added water, as the analyst could now say with

certainty whether a poor milk was naturally so, or had been made so by the addition of water. It is significant that very soon after the introduction of this test, the average solids not fat in milk, sold in Wellington, rose from 8.4 to 9.1 per cent and has remained at the latter figure.

The second great advance was the introduction of the reductase or methylene blue reduction test for ascertaining the bacteriological condition of milk. The findings from this test have resulted in a great improvement in the bacteriological quality of milk sold throughout the Dominion, and this must have had a beneficial effect on the health of children in particular. The Dominion Laboratory took a leading part as far as the British Empire is concerned in adopting the freezing point and the reductase tests and both were in regular use here many years before they were employed in Great Britain.

Pasteurised milk is required to be milk which has been held at a definite temperature for a definite time, but although this has been the law for many years the analyst had, until the recent introduction of the so called Phosphatase Test, no means of ascertaining whether this had been done. He can now do so with certainty. Thanks to the use of the freezing point, reductase, and phosphatase tests a control can be exercised over milk supplies which was impossible thirty years ago.

Although so much has been accomplished in curtailing the ordinary forms of adulteration, the present position is in several directions somewhat disquieting. The everyday shameless exploitation of "vitamins" could probably be largely curtailed by a stricter control of advertising, but the analyst can contribute little until practicable laboratory methods are available for determining the proportions of vitamins present in foods and drugs. Such methods will probably be available in the future.

The claims that are commonly made for many proprietary medicines and certain foods are a disgrace to a so called educated community. In this case also much could be done by a stricter control of advertising and particularly by requiring the composition of such medicines to be declared. This requirement would in itself have considerable effect in preventing exaggerated claims being made and would also enable the analyst to check up any statements made as to the components of the medicine. It is often impossible for the analyst to determine exactly the composition of an unknown medicine but it is comparatively easy to ascertain if a mixture has been made up to a declared formula.

The writer is of the opinion that until the law is altered, as suggested above, and rigidly enforced, the analyst can render little help in combating the exploitation of the public by the sellers of certain proprietary medicines.

A matter of considerable difficulty is the presence of traces of various metals in foods. In this case, thanks to the satisfactory methods now available, the analyst has no difficulty in obtaining reliable figures as to the amounts present in any food. The difficulty lies in the lack of agreement in regard to the amounts which may be harmful to health. There can be no doubt that in the future increasing attention will be paid to the question of trace amounts of metals in foods and in this work the analyst must take an important part.

The question of preservatives in food is also a difficult one and although the law is strict there is sometimes an effort made by interested people to have the law relaxed. The analyst must always be on the alert in case prohibited preservatives are added to foods. The modern practise of adding colouring matter to foods is strictly controlled by regulation, only certain foods are allowed to be artificially coloured, and only certain specified colours can be employed. However, in view of the possibly harmful effects of even minute quantities of certain of the synthetic colours the practise of artificially colouring foods should be discouraged and the varieties of colours used restricted to the lowest possible number of those which can, with a reasonable degree of certainty, be regarded as harmless.

I have endeavoured in this short paper to indicate that the analyst in New Zealand has done much to curtail the sale of adulterated foods and drugs but that new and difficult problems remain for him to meet.

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CHEMISTRY IN THE COAL AND GAS INDUSTRIES.

H. RANDS and F. J. W. BELTON

A century ago the early settler in New Zealand met his modest fuel needs by attacking the native bush with an axe. Today the most exacting domestic and industrial fuel requirements can be satisfied by simply turning on a tap. In this transition from the primitive to the modern, chemical science has played a large and essential part.

Extensive coal deposits were discovered in various localities very soon after organised settlement began, but the coals mined were found to be extremely varied in character and quality. Their classification, based mainly on the results of chemical analysis, was essential in order that the correct type of coal might be selected for specific purposes. Furthermore, coal from a particular mine, or sold under a particular name was by no means always of invariable chemical composition, and routine analysis of consignments became necessary for the protection of both supplier and consumer.

From at least as early as the "sixties" until the present day, analyses from these two points of view (classification and quality) have been carried out by chemists associated with various Geological Surveys, Schools of Mines, the coal-mining companies, and the large industrial consumers of coal.

In addition to these countless routine analyses, a considerable amount of chemical research work of both scientific and technical interest has been carried out, particularly on the lignites. While it is impossible in this brief summary even to list the investigations or the workers in this field, reference should be made to a considerable body of work extending over a long period of years, carried out personally by Professor W. P. Evans and by students under his direction at Canterbury University College. It has covered a wide field including such subjects as the vegetable structure, the sulphur and ash content of the lignites, and their use in gas producers and for low temperature carbonisation. At the Dominion Laboratory also, one or more research chemists have been engaged almost continuously for many years past on various problems concerning the efficient utilisation of our indigenous fuel supplies.

A "Summary of Investigations on New Zealand Coals" by W. Donovan, M.Sc., F.I.C., Dominion Analyst, containing also a bibliography, was published in 1928 as Bulletin No. 8 of the Department of Scientific and Industrial Research. Since the

date of this publication, further chemical research has been carried on, and a complete physical and chemical survey of the coal resources of the Dominion has been commenced. This vitally important work, the purpose of which is to obtain complete information on our coal reserves, to correlate coal seams of various localities, and to estimate the suitability of the coals for various industrial uses, is being carried out by a special chemical staff at the Dominion Laboratory, working in conjunction with a geological field staff.

The scientific investigation of the nature of our coal resources outlined above would have been of very little use had it not been paralleled by the application of scientific knowledge to the utilisation of the coal available. In this connection it is realised today that the mere release in useable form of the heat produced by the combustion of coal does not necessarily constitute the most useful or economical way of utilising the material. The progress of the science of chemistry has caused the Gas Industry to grow from an industry which merely carbonised coal for the purpose of producing a gas which would burn with a highly luminous flame, into an industry which has become the principal medium by which the wonderful potential resources of coal are being utilised in a manner increasingly beneficial and valuable to mankind in every walk of life. Nowadays the carbonisation of coal, as it is called, can be carried out in a variety of ways in order to obtain from the coal available the maximum yield of any particular type of product or to obtain the maximum yield of a variety of products of general utility. To put it more concisely, coal today can be so treated as to convert the whole of it into gas of a calorific value suitable for use as a town's gas or it can be treated so as to yield the maximum amount of coke of any particular type desired, together with a corresponding yield of gas and liquid products.

For a considerable number of years the maximum amount of research has been devoted to the development and utilisation of the materials obtainable by various chemical means from the liquid products of the carbonisation of coal, known in the crude state as tar; and in addition to the tar, large quantities of benzene and other aromatic hydro-carbons are recovered from the gas itself. The oils obtained from tar are chiefly of aromatic or unsaturated nature, and form the raw materials, the working up of which is today one of the most important branches of the chemical industry. The products obtained from these oils enter into every phase of our civilised life, and continually, ways are being found of converting one or other

of these materials into new substances for the benefit of mankind. Not only are these oils the source of very valuable motor fuels, the raw materials for wide series of dye-stuffs, drugs, and photographic chemicals, but also one of the chief sources of raw materials for the immense new industries of synthetic resins or plastics. It has been found that the tar acids used for disinfectants can, by appropriate chemical treatment, be converted into new substances having very greatly increased germicidal powers.

Nor is that the whole of the story; for, while the future of the hydrogenation of the coal which has so captured the public imagination, is very much in doubt, other processes have been evolved for the production of motor fuels and lubricating oils, using coal as the raw material. In these processes the coal is first converted into carbon monoxide and hydrogen, and then these gases are passed under controlled conditions over certain catalysts which promote a series of chemical reactions between the two gases, resulting in the formation of a wide range of oils. Even more remarkable still is one of the latest results of the researches constantly being carried out, in which it has been found that without the aid of a catalyst, under properly controlled conditions, coke may be directly hydrogenated with the production of hydrocarbon gases and some liquid products. This work is at present in the very earliest stages of development but its possibilities are extraordinary. The importance of this work will be best understood when it is realised that while the natural oil resources of the world are likely to have only a very limited life, the already known coal resources of the world are sufficient to last for many hundreds of years.

Of almost equal importance is other little known work which has been carried out at some universities on the production from coal of coke which is very highly reactive; at the same time, the problem of driving motor transport vehicles with producer gas is rapidly being solved, and so these two pieces of work conjoined, may yet be the greatest contribution towards releasing civilisation from the fear of the results of the drying up of natural sources of oil.

This brief outline will serve to give some slight indication of the services which coal and chemistry are giving to civilisation.

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CERAMICS.

O. C. STEPHENS

By Ceramics we understand ware of any kind, made from clay, and hardened by fire. It can be divided roughly into five main classes:—

(a) *Permeable Ware*.—1, Terracotta; 2, Refractory Ware; 3, Earthenware.

(b) *Impermeable Ware*.—4, Stoneware; 5, Porcelain.

No system of classification is entirely satisfactory as the classes merge one into the other.

Terracotta is the artistic development of the common red brick. The body is usually rather soft, but sometimes is as hard as steel. It is unglazed and the colour varies from buff to reddish brown.

Refractory ware includes all ceramic material that shows no sign of fusion when heated to 1550deg. Centigrade.

Earthenware includes all permeable pottery with a coating of glaze.

Stoneware is a slightly coloured, opaque, impermeable body. It breaks with a conchoidal fracture.

Porcelain (including chinaware) is pottery with a translucent white body, often showing a greenish tinge. It has a granular fracture.

The important raw materials are clay, a fluxing stone such as felspar, or Cornish stone, and silica in the form of flint, to which may be added such substances as steatite, cryolite, calcium carbonate, etc.

Clay has the general theoretical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. It can be divided into ball clay, China clay and fire clay.

Ball clay is a sedimentary clay, the chief characteristic being its high plasticity when treated with water, and on the existence of this plasticity depends the secret of clay working.

China clay is coarser in the particle than ball clay and is a residual clay formed by the weathering of granites. It fires to a pure white.

Fire clay is usually high in silica, low in alkalis, and is generally found in conjunction with coal measures.

When heated, clay loses its hygroscopic water at slightly over 100deg. Centigrade. Combined water is driven off from 350 to 600 deg. Centigrade. At about 800 deg. the silica and

alumina begin to form a new compound, mullite $Al_2O_3SiO_2$, the combination appearing to be complete between 1100deg and 1200deg. Towards 1500deg. Centigrade, vitrification commences. Any alkalis attack the aluminium silicate and form double silicates of potash or soda and aluminium.

Felspar is usually the potash spar containing 14.5 per cent to 16 per cent K_2O . It fluxes from 1100 deg. Centigrade and binds the body particles together.

Cornish stone is a weathered granite in which the decomposition has not proceeded to a finish. It also acts as a flux.

Flint containing 99 per cent silica is used in the body to form a refractory skeleton and also to balance the co-efficient of expansion of the body and glaze.

Manufacture.—In the preparation of the body, the dry materials are mixed with water in a blunger, then lawned through a 60 or 120 lawn, filter pressed and pugged. Then the article is made by (1) throwing; (2) pressing; (3) jollying; (4) casting.

In throwing, the clay ball is rotated on a potter's wheel, and the clay shaped by the hands of the potter. The actual origin of the potter's wheel is unknown, but it dates back thousands of years. There is ample evidence that it was used by the Persians, Hebrews and Egyptians.

The jolley is a modified potter's wheel, used in conjunction with a metal profile.

Pressing is done with either plastic or semi-dry clay, using phosphor-bronze dies.

Casting.—Casting slip is prepared by balancing clay and water by using definite quantities of sodium carbonate and sodium silicate. Such slip should weigh from 35 to 36 ounces per pint, and when poured into plaster moulds should not gel, but remain fluid. When the surplus is poured out a uniform thickness of clay is left round the interior of the mould, which should separate from the plaster. The proportions of sodium carbonate and sodium silicate vary for different clay mixtures.

When the ware is made it is carefully dried. If the surface rate of drying is not balanced by the movement of water from the centre outwards, cracks will form owing to differential shrinkage. The ware is then given its first or "biscuit" fire, the temperature depending upon the class of ware being made. It is then ready for decorating and glazing.

Decorating.—Although ordinary metallic oxides mixed with flux can be used (iron for brown, copper and chrome for

greens, cobalt for blues, etc.) the colours for decoration, whether used under the glaze, or on the glaze, are usually prepared by fritting, where the colours and the flux are wholly or partially melted by firing and then finely ground.

For underglaze painting, the colours, mixed with a special oil are painted on the "biscuit," the oil medium being fired off before the glaze is applied, or they can be applied using glycerine as the medium, over which the glaze can be directly sprayed or dipped, thus avoiding one firing. Such colours must of course be able to stand the full temperature needed to mature the glaze over them.

For on-glaze decoration the fritted colour, mixed with tacky turpentine, is painted on the glazed ware, and hardened on by a special firing, usually about 800 deg. Centigrade.

Glazing.—Glazes consisting of lead oxide, felspar, Cornish stone, flint, borax, calcium carbonate, cryolite and many other substances can be compounded to mature at a wide range of temperatures—from the lower majolica glazes up to the hard fired porcelain glazes. Where material soluble in water is used, it must be incorporated in the glaze as a frit which renders it insoluble, as all glazes are used as suspensions in water.

The glaze is applied to the biscuit by dipping or spraying.

Glaze Firing.—The composition of the glaze varies according to the temperature at which it is required to mature. For temperatures below 1200 Centigrade, lead glazes, or lead borax glazes are used, and above 1200 Centigrade, felspathic glazes.

Glaze differs from glass only in the higher alumina content necessary to meet the differing conditions. The essential oxides, apart from stains, are practically confined to those of lead, sodium, potassium, calcium, barium, magnesium, aluminium, boron, silicon, and phosphorus.

A glaze must have practically the same co-efficient of expansion as the body so that it will neither "craze" nor peel—although some crazed ware is beautiful and is much sought after by connoisseurs. It must be sufficiently viscous to hold to vertical surfaces, and yet flow smoothly on flat ones. Glazes may be clear and glossy, or else crystalline and matt. The matt glazes are made by the addition of titanium oxide, zinc oxide, or manganese dioxide to the glaze, sufficient being added to cause crystals of titanium—or zinc, or manganese silicates—to form on cooling, slow cooling favouring the formation of larger crystals.

Temperature Control.—Temperature is controlled by the use of pyrometers, or pyrometric cones. These pyrometric cones are about 2 inches high and are made of material similar to

the ceramic body. Chemical action, due to the heat, causes them to soften and bend at definite temperatures.

In the firing of porcelain the chemical reactions are not allowed to proceed to a finish (which would produce a glass) but are arrested when they have reached the desired degree, so that the time taken by the firing must be considered as well as the final temperature reached. For this reason pyrometric cones are a better indication of the finishing point than pyrometers, which merely indicate the final temperatures.

Clays in New Zealand.—Clay deposits in New Zealand fall into three main classes:—

- (1) Residual Clays. These, with varying felspathic content, are found in many parts, but mainly Auckland.
- (2) Glacial Clays. These are to be found at Kaikorai, Wingatui and Wellington.
- (3) Tertiary marine clays. These are to be found over wide areas in the North Island, from Wairarapa, Waikaremoana, to the East Cape; and in the South Island at Collingwood, Takaka, Pareora, and Waikouaiti.

Fireclays are found usually in association with coal measures.

Highly aluminous clays containing kaolin, varying from 80 to 95 per cent, occur with varying proportions of felspar at Kakahu (South Canterbury), Nelson, New Plymouth, Whangarei, Mount Somers and other places.

The Kakahu, Nelson and Whangarei clays are being used with success in the manufacture of glazed earthenware, and also of stoneware. The percentage of iron and titanium in these clays is usually sufficient to colour the body when fired.

Refractory Clays.—There are few deposits of first grade clay in New Zealand and when they do occur they are usually in small quantities. The best is to be found in the Mount Somers district, and there is also a good clay at Charleston. These refractory clays are being used in the manufacture of fire bricks and furnace linings.

Stoneware clays are found at Glen Massey, Whangarei, Nelson, and in Otago and Canterbury. Some of these are being used in the manufacture of glazed pipes.

Brick-making clays occur over wide areas in both Islands and there are many factories making bricks and tiles.

Of fine glazed decorative earthenware, or china, there is little being made, but a number of amateur potters in Auckland, Wellington, Havelock North, Dunedin and elsewhere, are producing good quality ware.

PORTLAND CEMENT IN NEW ZEALAND.

E. LEESE

Portland cement was first made in England 115, and in New Zealand 54 years ago. The forerunners to portland cement were hydraulic lime, natural, Roman and pozzuolanic cements. Of these only hydraulic lime was made in New Zealand. Certain specialised non-portlands have been manufactured in a small way, and such types include oxymagnesium chloride cement. Aluminous cements have received no attention in New Zealand owing to the absence of suitable alumina deposits.

The first recorded New Zealand hydraulic lime was that made by J. T. Thomson, Provincial Engineer, Roads & Works, who used Moeraki Boulders as raw material in 1868, and his product was used in the Oamaru breakwater in 1873. Nathaniel Wilson of Warkworth, was also experimenting with and producing hydraulic lime between 1865 and 1870, and in 1876 was selling his product in Auckland in competition with English portlands. John Wilson & Co. was formed in 1878 and in 1885 this Company manufactured commercially the first portland cement in Australasia. This was at Warkworth, using vertical kilns with coke firing—capacity of plant, 600 tons per year.

Rutherford Bros., in 1884, made hydraulic lime at Limestone Island, Whangarei, and James McDonald produced cement in Dunedin in 1886. The Milburn Lime & Cement Company was formed in 1889, the first year's output being 950 tons.

The New Zealand Portland Cement Company (Limestone Island) was formed about 1901, and Golden Bay Cement Company in 1909. The Dominion Cement Company, Whangarei, commenced operations in 1913. In 1918 the Wilsons, New Zealand and Dominion companies amalgamated, centralising operations at Portland, near Whangarei. This left three factories operating in New Zealand, the Milburn Company in Dunedin, Golden Bay Company in Nelson, and Wilsons at Whangarei.

The total annual production of portland cement in 1900 was 3,000 tons; 1912, 50,000 tons; and 1939, above 200,000 tons.

Outstanding events in the history of the industry are as follows:—

First rotary kiln, Warkworth, 1903, using pulverised coal for burning.

First Chemist appointed 1899. Milburn Works Dunedin.

First standard specification for cement (English) 1904.

This specification was followed by New Zealand manu-

facturers, also the amendments of 1907, 1910, 1915, 1920, 1926, and 1931.

New Zealand Standard Institute formed in 1933.

First New Zealand Cement Standard adopted 1935.

Wet process cement-making started in 1928, by Wilsons, Whangarei.

Rapid-hardening cement first made 1928-29. First job on which rapid-hardening cement was used—High Street paving, Auckland. Road opened for traffic 30 hours after concrete was laid, 1929.

The portland cement industry is one in which chemical control has played a vital part during the past forty years, and it is probably the first to adopt continuous chemical control in manufacturing. The futility of trying to produce a reliable cement without the aid of technical chemists was early recognised.

Portland cement is a product resulting from burning to incipient fusion a correct mixture of silica, alumina, iron oxide and lime, and pulverising the burnt material to an impalpable powder with added retarders. The raw materials in nature are sedimentary shales and limestones which vary considerably in required constituents. It is the chemist's job to correctly adjust all irregularities, to mix suitable natural products by blending, and control grinding to obtain intensely fine particle subdivision and dispersion. This is followed by burning the filtered raw slurry in rotary kilns at 3000 deg. F, with specially selected and pulverised coal.

Close control of this point is vital as decomposition and complete chemical recombination of bases and acids must be continuously obtained. The products following correct burning are tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite, with no free lime. It is by a judicious interpretation of the percentages of each ingredient required in the finished cements that the particular properties desired for various purposes in use are attained. These properties include speed of setting and hardening, capacity to combine and harden in air and under water with a maximum of aggregate and strength.

Cement making is a continuous process and chemists are therefore following each stage in manufacture all the time. Cements made in New Zealand are equal to those produced anywhere, and it has taken many years of patient work for the present system of control and quality of products to become a possibility. The early laboratories were poorly equipped and