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THE BRANCHES, 1936—

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The New Zealand Institute of Chemistry (Inc.)

COUNCIL, 1937.

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JOURNAL

of the

NEW ZEALAND INSTITUTE OF CHEMISTRY

EDITORIAL

A MATTER OF POLICY.

A questionnaire is a notoriously difficult document both to construct and to answer on simple lines so that the essential issues may be clearly expressed and clear, positive answers evoked. The questionnaire which members of this Institute answered a short time ago has given a clear indication of the policy which members desire the Publications Committee to follow. For this direction the Committee is profoundly grateful.

During the months following our first issue there were numerous and frequent controversies among our members upon all questions affecting this *Journal* often displaying vital and fundamental cleavages of opinion. As a result, the Publications Committee was reluctant to begin handing material to our printer, and much less to release the present issue until it knew with some degree of certainty what the considered opinions of our members actually were. It was hoped that the deliberations in Conference at Auckland might have crystallised average opinion, but it was decided, on the authority of Council, to conduct a postal ballot. Information was desired on three points: (1) Whether the best interests of our Institute are served by the regular publication of a journal, (2) Whether members would actively support such a publication, and (3) What type of material is most desired.

Sixty-nine replies were received, the number clearly representing a true cross-section of our membership. To *Question 1* ("Do you consider the best interests of our Institute are served by the regular publication of a Journal?"), the replies were: Yes, 57 (83%); No, 10 (14%); Unanswered, 2 (3%). To *Question 2* ("Would you be prepared to assist where possible in contributing articles, etc.?"), the replies were: Yes, 55 (80%); No, 8 (11%); Unanswered, 6 (9%).

In *Question 3,* members were asked to place eight proposals in order of preference, and opinions were assessed by awarding seven votes to the first choice and none to the last choice. The voted order of preference was as follows:—

Question:		*Votes*:	*% of Total Votes Cast*:
(b)	Articles of general Chemical interest	321	17.6
(d)	Papers delivered before Branch meetings (if not published under a, b or c)	273	15.0
(c)	Notes on laboratory technique	262	14.4
(g)	Official notices from Council; business at Council and Branch meetings, etc.	240	13.2
(f)	Full account of Conference	239	13.2
(a)	Papers of original research	203	11.1
(e)	General news of Branch activities and matter not scientific	197	10.8
(h)	Book reviews and general	85	4.7

This summary of the questionnaire calls for little comment. It must, however, be recognised that the obvious difficulties with which a scientific society in our young and scattered community has to contend render it most urgent that all who answered the first two points affirmatively should follow up by personal action their mandate to develop our own *Journal.*

* * *

We desire to offer hearty congratulations to Dr. J. C. Andrews (Auckland) and to Dr. R. O. Page (Christchurch) on their appointment to the Council of Scientific and Industrial Research. Our former President, Professor H. G. Denham, has been Chairman of this Council since 1935, and both he and Mr. T. Rigg have been members of the Council since its formation in 1926.

* * *

Mr. W. Donovan, Director of the Dominion Laboratory and Dominion Analyst, has been seriously indisposed for the past year. Mr. Donovan underwent a major operation and suffered relapses during convalescence. All danger now appears to be past, and we are glad to report that he is now well on the road to recovery.

* * *

Our sympathy is extended to the Hon. General Secretary, Mr. T. A. Glendinning, in the death of his wife at the beginning of this year. Mr. Glendinning has himself recently suffered ill-health but is now recuperating before resuming his valuable services to the Institute.

BOOK CONCESSIONS.

The Publications Committee, with the approval of Council, has made arrangements for *bona fide* members of the Institute to obtain reference and other books on advantageous terms. Publications which are ordered by members through the Book Department of Messrs. Technical Publications Ltd., 22-24 Brandon Street, Wellington, C.1, " will be charged to the person concerned at the rate of 25% to 33⅓% on the English published price, according to the publishers. These percentages are to cover the Exchange Rate, Bank Charges, Landing Costs, Postages, etc."

The firm has undertaken that, if at any time it finds itself unable to supply a publication at the above rates, it will notify the person concerned before accepting the order.

The Committee requests that Associates and Fellows should avail themselves fully of this privilege, for the measure of success attained will govern future extensions of the scheme to a wider field of chemical and technical literature. An active policy in this connection is being developed (we have in mind, for example, the Bibliofilm Service of America) and members are invited to make suggestions to the Editor either direct or through the Branch Sub-Editors. Neither the Institute nor this Committee has in any way committed itself in this matter, the whole basis of the negotiations having rested upon mutual advantages. Always mention this *Journal* when ordering.

NEW ZEALAND STANDARDS INSTITUTE.

A noteworthy event occurring during the recent expansion of the activities of the Department of Scientific and Industrial Research has been the reorganisation of Standards Development under State Control. The New Zealand Standards Institution dissolved in August 1936, and was reconstituted under the amended title of the New Zealand Standards Institute. The new organisation appears to have settled down as an integral part of our industrial structure and is living up to expectations with the increased facilities at its disposal.

The unification and co-ordination of standards with systematized references on a basis that secures their wide application as national standards constitute an activity of such industrial, economic and social import as to be sufficient warrant for its being undertaken as a legitimate Government activity, more especially in a Dominion like New Zealand where business, trade and industrial organisations are insufficiently organised to offer any effective alternative. That this is appreciated by the Executive of the overseas Standards organisations is indicated by the following extract from the " Financial Times," London:

> "The beneficial nature of the work of the British Standards Institution has become so well established that it is a moot point whether it should not be accorded wider powers. There can be no doubt that it has to sacrifice a good deal at times to conciliate fractious opposition and petty vested interests, to the great harm of industry generally, especially when dealing abroad."

On the formation of the Institute, the Hon. the Minister of Scientific and Industrial Research immediately appointed an Advisory Council consisting of twenty members representing State Departments, Local Authorities and private, industrial and trade organisations. (The N.Z. Institute of Chemistry is officially represented on this Council). This Council meets each alternate month. We understand that there will also be appointed three district Advisory Committees in Auckland, Christchurch, and Dunedin to ensure that close contact is maintained on a national basis. At the first meeting of the Advisory Council in September, 1936, certain Committees were appointed and at the present time there are forty-five of these functioning with some three hundred members.

Those Committees in which our Institute members will be most closely interested are:

No. 5. *Chemical Divisional Committee.*—Responsible to Advisory Council for consideration of all standards projects.

No. 6. *Dairy Machinery and Requisites Standing Committee.*—All standards relative to Dairy Industry.

No. 9. *Consumer Standards Standing Committee.*—Development of consumer standards for domestic and household requirements.

No. 10. *Testing Facilities Special Committee.*—Investigate and report upon testing equipment available in New Zealand and to prepare representations urging the establishment of a National Physical Laboratory.

No. 12. *Primary Products Special Committee.*—To report on standards for these as requested by the British Standards Institution.

The above and other Committees are now considering projects covering such diverse fields as paints and coatings, steel, dry cells, salt and acidity in butter and cheese, dairy sterilisers—colouring and rennet, refrigeration, specifications for chemical substances and apparatus, paper, frozen lamb and mutton, hides and leather goods, woolpacks, citrus fruits, catalogue of testing equipment, etc.

Over 200 draft specifications have been reviewed already by the several Committees and over 900 copies of these have been circulated among 2,000 affected parties. These interests forward their comments which, after correlation, are the basis recommendations made to the Advisory Council for the adoption, amendment or rejection of the drafts so far as New Zealand is concerned. Ultimately these drafts may become New Zealand Standards, subject to final endorsement by the Minister of Scientific and Industrial Research. Up to the present time 77 draft specifications have been recommended for adoption as New Zealand Standards and six others have been actively adopted as New Zealand Standards.

The Institute welcomes enquiries from interested parties, and individual members of the New Zealand Institute of Chemistry may wish to communicate with the Secretary on subjects of importance to themselves. To supplement its services, the Standards Institute maintains a comprehensive card-index as a key to information contained in specifications and reports from the main Standards organisations overseas.

NOTICES.

Conference: The combined Annual Conference of the N.Z. Institute of Chemistry and the Institute of Chemistry of Great Britain and Ireland will be held in Christchurch on January 20 and 21, 1938.

Change of Address: Members are earnestly requested to acquaint the Hon. General Secretary with any change of address without delay.

Transfers: Members who wish to transfer from one branch to another must notify the Hon. General Secretary to that effect and must pay the current subscription; except under these conditions, no transfer will be made.

Leave of Absence: This can only be granted to those members who apply to Council and whose subscriptions are paid for the current year. Members who do not so apply are liable for all unpaid subscriptions.

Membership: At the close of the 1936 session, there were 162 members—an increase of 13 over the previous year. Of these, 20 were Fellows. The corresponding figure for 1937 was 161, of whom 25 are Fellows.

Registration: Council had under consideration the registration of the Institute as a Union; after full discussion this proposal was rejected by the Branches. The draft of a Bill to provide for Registration by Act of Parliament has been engaging the attention of the Branches.

Standards: A Committee has been appointed to co-operate with the N.Z. Standards Institute.

Salaries: Cases in which members of the Institute are considered to receive inadequate salaries have been brought to the attention of Council, which proposes to act in the interests of members wherever possible.

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THIS JOURNAL.

Any article may be reproduced from this *Journal* provided due acknowledgement (including author's name) is made.

No responsibility is accepted for the accuracy of statements made by contributing authors.

All communications regarding this *Journal* should be made to *The Editor* either direct or through a local Branch Editor. The personnel of the Publications Committee is being increased in order to ensure the more rapid handling of our activities.

Members and others are invited to contribute scientific articles or general matter of interest to the profession in New Zealand: these will be welcomed at all times. It is intended to publish the next issue of this *Journal* in February, 1938, to contain a full report of the forthcoming Conference proceedings and also Branch activities during the 1937 session. It is, therefore, urged that all material for publication should be to hand before the middle of February next.

Notice to Authors: 1. Unless all material submitted for publication is in typescript or very legibly written, the Publications Committee can accept no responsibility for inaccuracies and may reject the manuscripts. Much loss of time has already occurred through this cause. Diagrams and chemical formulae should be sparingly employed.

2. References to the literature are to be arranged as shown in this issue of the *Journal*. Titles of reference books must be given in full, with edition and date. As to current periodicals, the only abbreviations acceptable are those adopted as an international standard by the International Union of Chemistry. These are used by the (British) Bureau of Chemical Abstracts and by the American Chemical Society. A complete reference index of journals and official abbreviations may be found in the last issue of American Chemical Abstracts for 1936, Vol. 30.

3. An author desiring extra copies of the *Journal* to which he has contributed an article should inform the Editor of the number required when submitting his manuscript.

ADULTERATION OF FOOD IN NEW ZEALAND.

R. L. ANDREW.*

The following is a sketch of the operation of the Sale of Food and Drugs Act in New Zealand for the last twenty-nine years, from the point of view of an analyst connected with its administration over the whole of that period.

The effective control of the adulteration of food is a comparatively recent development. The reasons for this are many, the chief being the modern development of the sciences and with it an enlightened public opinion, resulting in sound legislation properly administered. In the early part of the 19th century several sensational books dealing with the adulteration of food were published in England. They attracted considerable attention and had a great influence on public opinion. In the light of present-day knowledge these books contain many gross errors, but after one makes due allowances they reveal an intolerable state of affairs.

In 1851 the Analytical Sanitary Commission was set up by the "Lancet." The principal worker was Dr. A. H. Hassal, and his book, "Food and Its Adulterations," was the first really scientific English work on the subject. The Commission was not lacking in courage for it publicly exposed many offenders. The "Quarterly Review" for March, 1855, states: "A gun fired into a rookery could not cause a greater commotion than did the publication of the names of dishonest tradesmen, nor does the daylight when you lift a stone startle ugly and loathsome things more quickly than does the pencil of light, streaming through a-quarter inch lens, surprise in their native ugliness the thousand and one illegal substances which enter more or less into every description of food which it pays to adulterate. Nay to such a pitch of refinement has the art of fabrication of alimentary substances reached, that the very articles used to adulterate are themselves adulterated, and while one tradesman is picking the pockets of his customers, a still more cunning rogue is, unknown to himself, deep in his own." As a result of these exposures several successive Acts were passed to deal with the evil, and finally the Sale of Food and Drugs Act was passed in 1875—and this with a few amendments is in force to-day.

Apart from the reports of the Colonial Laboratory the writer has been unable to discover what action was taken in the early days of New Zealand. In 1870 a select report of the House of Representatives states that various foodstuffs had been examined. Almost all the coffees were adulterated; two could only be regarded as foreign substances, slightly adulterated with coffee. In 1874, a special report on articles liable to adulteration states that of fifteen samples of tea all were adulterated. The green teas were "faced" with prussian blue and chromate of lead. Of seven samples of mustard, five were

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adulterated. The above information, though meagre, indicates an unsatisfactory state of affairs. Various Acts were passed until they took final form in the Sale of Food and Drugs Act, 1908. This Act is modelled on the English Act. The administration of the Act is a function of the Department of Health, and brief mention is made of some of the pertinent provisions.

Section 5 gives power to demand, select, and take samples. Section 7 lays down the procedure to be observed in taking samples. The sample is to be divided into three parts, one to be offered to the seller, one delivered to the analyst, and one retained by the officer taking the sample. In New Zealand the "Analyst" is a full-time Government Analyst on the staff of the Dominion Laboratory. In England samples are analysed by "Public Analysts" who are not Government servants, but are in private practice. The New Zealand practice is the better for our conditions.

Section 12 defines offences under the Act, and Subsection 1 reads: "Every person commits an offence who sells any adulterated food or drug without fully informing the purchaser at the time of sale of the nature of such adulteration, unless the package has conspicuously printed thereon a true description of such food or drug." The proviso in this Subsection is never availed of, because people will not knowingly buy adulterated food, and also because Subsection (8) provides that the provisions of Subsection (1) are subject to such exceptions as are prescribed by Regulations under the Act, and these Regulations are so complete that they cover practically all foods. Section 15 (a), (b), and (c) define adulteration with legal minuteness and Subsection (d) says a food is adulterated if it does not comply with the standard therefor prescribed in Regulations made under the Act.

In legal proceedings action is almost always taken for a breach of the Regulations and not directly for a breach of the Act. It is here that our procedure differs from that generally followed in England, where with certain exceptions, the question of the purity of food is decided by the Magistrate after hearing evidence. In N.Z. the standards of purity are set out in the Regulations and the Magistrate is required only to decide from the evidence whether or not the Regulation has been complied with. The following example illustrates the difference: In England a butcher sold sausages containing only 43 per cent. of meat and was proceeded against on the grounds that a sausage should contain at least 50 per cent. of meat. The Court had no legal standard before it, and after hearing lengthy argument the case was dismissed. In New Zealand the seller would have been convicted, as the sausages did not contain 75 per cent. of meat as required by Regulation 36 (10).

An amendment to the Act was passed in 1924. This contains an important provision which makes it an offence to publish in a newspaper or in any other manner anything which directly or by implication qualifies statements required on labels by Regulations under the Act. For instance, "coffee and chicory," which must be so labelled on the container cannot now be advertised as coffee.

We now come to the Regulations under the Act. They follow closely the Federal (U.S.A.) Food Standards and those of the Australian Commonwealth. The first complete set of Regulations was gazetted in 1913, and as necessity arose they have been subjected to fairly numerous amendments. Under the heading "General Regulations" many technical requirements regarding labelling are defined. Regulation (3) forbids misleading statements on labels and reinforces a similar provision in the Act.

The indiscriminate addition of preservatives to food would be a real menace to the public health as they are in no case foods, they may be poisonous, and may be used to conceal incipient decomposition. The use of preservatives is therefore very strictly controlled. Regulation 12 (1) states that: "The addition of a preservative substance to any article of food except as specifically permitted is hereby prohibited." In the special cases where preservatives are allowed only certain specified preservatives may be used, the amount is strictly limited, and its presence must be declared. The preservatives allowed are benzoic acid, salicylic acid and sulphur dioxide. The traditional preservatives, salt, saltpetre, sugar, spices, wood-smoke, vinegar and acetic acid are not regarded as preservatives for the purposes of the Regulations.

It has been the custom from time immemorial to add colouring to certain foods. In former times some of the colourings used were poisonous, e.g., lead chromate and copper arsenite, but it is doubtful if any of the colours employed to-day are harmful to health. The chief objection to their use is that they may conceal inferiority or give a false appearance of superiority. Regulation 11 (1) forbids the addition of colouring to foods except as specifically permitted. With some exceptions, where colouring is added its presence must be declared. The permitted colours include caramel, saffron, chlorophyll and every innocuous vegetable colour extractive and a number of specified coal tar colours. The latter are particularly suitable as they give bright results, and a little goes a long way. They are, therefore, the most generally used.

The possibility of food being contaminated with poisonous metals is guarded against by requiring adequate precautions during manufacture and storage. There is little chance of any foodstuff containing dangerous quantities of poisonous metals, but constant care is necessary. Regulation (13) requires that no food shall contain any antimony, arsenic, lead, tin, or compound of any of them. It shall not, however, be a contravention of this Regulation if certain foods contain not more than specified amounts of arsenic, lead, or tin, provided that such metals are unavoidably present in such foods. Various tinned foods may contain not more than two grains of tin to the pound or pint (as the case may be). It must be remembered that tin is not toxic except in large quantities. Lead is allowed in certain foods in quantity not exceeding one seventh of a grain to the pound or pint.

Not more than 1/100 grain of arsenic per pound is permitted in apples and pears. This is to allow for unavoidable traces of arsenic which may remain on the fruit after spraying. Before this was allowed, a thorough investigation was made and it was found that with ordinary spraying practice, and provided there is an interval of twelve to fifteen days between the last spraying and the picking, there is no risk of the arsenic being in excess of 1/100 grain to the pound. The amounts found in peeled fruit are so small that they may be regarded as of no significance.

Not more than 1/100 grain of arsenic is allowed in ale, beer, and stout. Any arsenic present would in all probability be introduced from the coke used in roasting the malt. Beer has been examined regularly over the last 28 years; in several cases the quantity of arsenic has been just on the maximum, and in one case it was slightly exceeded. By attending to the coke even this small amount was eliminated. It is usual for the beers examined to contain no detectable amount of arsenic.

Arsenic is allowed in a few other foods in quantity not exceeding 1/100 grain to the pound or pint. It should be added that with the exception of apples and pears, and ale, beer and stout, the foods in which these small amounts of poisonous metals are allowed are not largely consumed.

We next come to the specific Regulations which include definitions, standards and labelling required for practically all foods. With many of these Regulations the Analyst is not directly concerned and in the remainder of this paper the writer deals only with items of special interest.

In the case of *flour* the only requirements causing difficulty are the prohibition of artificial bleaching and of the addition of chemical improvers. Artificial bleaching is resorted to meet a real or fancied demand for a very white flour. A variety of agents may be employed but the most usual is nitrogen peroxide or chlorine. Their bleaching action is due to destruction of the carotene or yellow colouring matter of the flour. It is certain that the nutritive qualities of the flour are not enhanced by "chemical bleaching," and in view of the relationship between carotene and vitamin A, it is very probable that such treatment is undesirable. The removal of the colour may also give the flour a supposed enhanced value and the buyer therefore may be prepared to pay more than he otherwise would.

Improvers are usually added to flour to increase its strength, as strong flours are more satisfactory from the bakers' point of view. The chemical improvers usually employed are calcium sulphate, acid calcium phosphate, ammonium persulphate, and potassium bromate. Acid calcium phosphate is the only chemical improver allowed in New Zealand.

Custard Powder is defined as a powder prepared from wholesome starch with or without harmless colouring or (and) flavouring matter. To effectively control this food it has been necessary to prohibit the word "egg" and expressions or devices which suggest the presence of egg from being written on the label of packages of custard powder. Some traders found it difficult to drop the old practice of selling this preparation with the suggestion that it contained egg.

Cream of Tartar provides an interesting example of the improvement brought about by strict control. The standard requires that cream of tartar shall contain acid tartrates equivalent to not less than 95 parts per centum of potassium acid tartrate, and not more than 1/7 grain of lead to the pound. Formerly a considerable proportion of the cream of tartar sold was rather dirty in appearance, contained only just 95 per cent. of acid tartrates, and more than the maximum permitted amount of lead. For many years the cream of tartar examined has contained 99-100 per cent. of acid tartrates, and was either lead free or contained mere traces of that metal, most of it being of "Analytical Reagent" standard of purity.

Baking Powder is described as a chemical leaven, and is required to yield not less than ten per cent. by weight of carbon dioxide on heating with water. When this Regulation was first enforced there were a number of inferior baking powders on the market; to-day it is safe to assume that all the baking powders sold are of high grade and will yield about 14 per cent. of carbon dioxide. Coloured baking powder is allowed, but it must not be labelled to suggest the presence of egg. Formerly this product was sold as egg powder, and in some cases such misdescription was abandoned with considerable reluctance.

In no case has *sausage meat* been found to contain less than the 75 per cent of meat required by Regulation. The preservative sulphur dioxide may be added to sausage meat and occasionally the quantity allowed is exceeded. With the widespread use of cool storage the use of this preservative could probably be abandoned by sausage makers without hardship to them and with benefit to the consumer.

With edible oils the most common breach is mislabelling. Peanut, cottonseed, and more recently soya bean oil have been sold as olive oil, which is the most expensive of the edible oils.

Milk is by far the most important food to the Analyst. This is reflected in the numbers examined. In 1934, 7921 milk samples were examined in the Dominion Laboratory and the three branches as against 1355 other food samples. There are several reasons for this; milk is very easily adulterated, as no skill is required to add water or to abstract fat; it is perishable and is soon disposed of, so that the adulterator knows that all trace of his guilt will be gone in a day. Our experience over thirty years has demonstrated the great value of strict control. When sampling was first seriously undertaken in 1910-1913 the samples analysed contained an average solids-other-than-fat content of 8.5 per cent.; it is now 9.0-9.1 throughout the Dominion. At first great objection was urged against the standard of fat, 3.25 per cent., solids-other-than-fat, 8.5 per cent. Investigations were made with the result that the standard was not modified. Subsequent experience has all been in the direction of supporting the decision to maintain the standard. The milk supplies of New Zealand are now, on the whole, most satisfactory, and it is now hard to realise how bad was the supply of Wellington and of some other parts of the Dominion some thirty years ago. Adulteration by watering and skimming was quite usual, and in summer it was not unusual for preservative to be added. The bacteriological condition of supplies was also most unsatisfactory. At first it was difficult to effectively deal with watering as no certain means were available for detecting less than seven per cent. of added water in an average quality milk. In 1912, however, the freezing-point test was adopted and vendors soon found that added water would be detected even if the amount added was not sufficient to bring the solids other than fat below the standard.

On the bacteriological side very little effective action could be taken until the Reductase Test was introduced about 20 years ago. In this test the comparative bacterial content of the milk is ascertained by its power of reducing methylene blue. It has the great advantage of simplicity and in addition gives on the whole more reliable data than the more complicated and expensive method of plating out.

Another advance in recent years has been the introduction of the Phosphatase Test for the control of pasteurisation. Previous to this, there were no reliable means of ascertaining whether or not a milk had been pasteurised and if so, for the required time and at the correct temperature.

No samples of condensed milk have been found adulterated but there was one very glaring instance of mislabelling in which ordinary unsweetened condensed milk was labelled "Evaporated Cream."

In New Zealand *butter* is never adulterated with foreign fat, but occasionally it is sold containing more than the maximum permitted amount of water (sixteen per cent.). It is, of course, profitable to sell water at butter prices. The preservative, boric acid, was formerly allowed in butter, in quantity not exceeding 35 grains to the pound (0.5 per cent.). It was held by some that the preservative was essential, but its prohibition has caused no hardship, and the consumer does not eat with his butter a substance which would possibly be injurious to health.

In none of the *teas* examined has any of the traditional adulterants in the form of foreign or exhausted leaves been found. Several samples contained an undue proportion of stalks and others contained sand, but these were very cheap teas imported for use by Chinese. In one isolated case an expensive "China" tea was found to contain an arsenical "facing" compound. The sellers were quite innocent and the tea was quickly taken off the market, but the laboratory has an exhibit illustrating an almost abandoned but once common practice.

It was not uncommon to sell a mixture of *coffee* and chicory as coffee, but this form of mislabelling is now very rare, the mixture being sold as coffee and chicory.

Ground White *Pepper* was usually mixed with ground rice, and more rarely cornflour or ordinary flour. This practice has long been abandoned and pepper is true to label. The most common breach with *vinegar* is mislabelling, sugar vinegar or other vinegar being sold as the more expensive malt vinegar. In one case tapioca was used in making vinegar, which was sold as malt vinegar, but the Magistrate ruled that it did not comply with the standard for malt vinegar, in that tapioca was not a cereal. In former days dilute solutions of acetic acid coloured with caramel were sold as table vinegar and sometimes as malt vinegar. Since 1913 such a product if sold as vinegar must be labelled "Imitation Vinegar" and must not be coloured. This preparation became much less popular when so described.

It is very doubtful if *jam* was ever adulterated with turnip and pumpkin, although as a boy, one heard that loads of these were seen at the jam factory. They would probably be dearer than and not nearly as effective as apple, and would probably be detected by appearance and taste. Formerly much of the jam was artificially coloured but this practice has long been abandoned. Mislabelling also is now practically unknown, and apple, when present, is declared on the label.

Vanilla Essence must be an alcoholic extract of vanilla bean. Essence thus prepared contains other flavouring substances in addition to vanillin, and it is the presence of the former that makes true vanilla essence superior to an essence prepared from synthetic vanillin. Solutions of synthetic vanillin can be sold but only as "imitation vanilla" or "imitation vanillin essence." It was formerly a common practice to mislabel these synthetic preparations as true vanilla essence.

In conclusion, the writer would emphasise the fact that during the last thirty years the traditional forms of adulteration and mislabelling of foods have almost entirely disappeared in this country. The most pressing problem with foodstuffs is therefore not so much the danger to health through wilful adulteration, as from the consumption of the wrong types of food, the possible harmful effects of over-refinement and of the addition of minute amounts of foreign material, as in the bleaching of flour and the treatment of various foods with preservatives, and also the probability of mineral deficiencies in the soils causing corresponding deficiencies in the plant and animal foods produced on them.

INDUSTRIAL EFFLUENT AND STREAM POLLUTION IN NEW ZEALAND.

F. P. WORLEY.*

One of the penalties of industrial development in other countries has been the destruction of the beauties of the countryside or the foreshore, the pollution of the air by smoke from factories and the conversion of sparkling streams into foul sewers. In New Zealand we are attempting, wisely or foolishly, to foster both by natural and by artificial means, a number of secondary industries. In fact, it is claimed that there are now very few things that are not already being manufactured in the Dominion. The largest and most important manufactures are those connected directly or indirectly with primary industries and it may be found profitable further to develop the processing of primary products for export. Secondary industries, other than those directly connected with primary products are not likely to develop, except in a few cases, beyond the stage of supplying part of the comparatively small local demand. Furthermore, such industries will in general be located in or near the main cities on the coast. It is important however, to recognise at the outset the disadvantages and dangers accompanying industrial development. Of particular concern to the industrial chemist is the danger of pollution of the atmosphere and of streams. It would undoubtedly be a tragedy if industrial development were allowed unnecessarily to destroy the natural beauties of the countryside or pollute the atmosphere. In many parts of England can be seen the tragedies of industial success.

The effluent from manufactures can be objectionable in three different ways. It may contain suspended solids which, in the course of time, may form deposits of an objectionable or deleterious nature on the beds or banks of streams or rivers or on the seashore, it may contain dissolved chemicals of a poisonous nature affecting plant and animal life, or it may contain substances in solution which, though not actually toxic, use up the dissolved oxygen of the water, making the water unsuitable for fish life. Ordinary domestic sewage in addition to its bacterial dangers has a marked effect in reducing the dissolved oxygen. It is estimated that the average five-day biochemical oxygen demand of domestic sewage per capita per day is equivalent to 0.167 lbs. of oxygen. If dilution is not sufficient, dissolved oxygen may be reduced below the minimum required for fish life, about 2 parts per million. Industrial wastes from dairy factories, canning works and pulp mills can be conveniently compared with domestic sewage as far as biochemical oxygen demand is concerned.

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*Portion of Presidential Address delivered by Professor Worley to the N.Z. Institute of Chemistry, Auckland, January, 1937.

The only manufacturing industries in New Zealand not located near the sea coast are those connected with dairying. Here there are undoubted problems with regard to effluent, but insufficient data are available for an analysis of the position. Pollution of streams has not yet been of a sufficiently serious nature to necessitate the appointment of a permanent committee, but it would probably be wise to appoint such a committee before trouble occurs, instead of waiting till the damage has been done.

A problem that will arise in the near future is the utilisation of the timber of the pine forests that have been planted by the Government and by private companies. These trees are approaching a size suitable for pulping and it may be found necessary to establish inland one or more pulp mills. Three of the most important methods of pulping are the mechanical ground wood, the sulphite and the sulphate processes. These differ not only in the nature and quality of the product, but also in the nature of the effluent from the mills and it is necessary to consider which process would be most suitable for our conditions both on economic and other grounds. From the point of view of effluent, the sulphite process is the least desirable. In this process the non-cellulose part of the wood, generally known as lignin, is dissolved out of the chipped wood in large digesters by calcium bisulphite solution. As the cellulose content of the dry wood is only about 50 per cent., and as none of the lignin products can, in general, be profitably recovered, the waste liquors will contain in solution about 50 per cent. of the wood treated, converted by the process into various chemical compounds, including sugars, alcohol, aldehyde, cymene, formic and acetic acids, etc. In addition there will be wood fibre and any inorganic chemical not retained by the recovery process. The biochemical oxygen demand of the effluent from a sulphite mill is equivalent to a population equivalent of about 1500 persons per ton per day of product. Thus, a mill producing 100 tons of pulp per day by the sulphite process would have effluent equivalent in oxygen demand to the domestic sewage from a city of 150,000 people. It is obvious that a sulphite mill of economic size should not be tolerated except on the sea coast.

The groundwood pulp mill has a comparatively innocuous effluent, the population equivalent being only 20 to 30 per ton of product. This process, however, is suitable only for certain purposes.

The sulphate process is theoretically perfect from the point of view of effluent. In this process the cooking liquor which dissolves out the non-cellulose part of the wood is a solution of caustic soda and sodium sulphide. When the cooking is complete the charge from the steel digesters is transferred to wash tanks or "diffusers" where the liquor, known as "*black liquor*" is washed out of the pulp. This "*black liquor*" is concentrated in evaporators and finally dried in a rotary furnace to a solid material known as "*black ash,*" which contains the greater part of the alkali used in the cooking process together with the charred organic matter derived from the non-cellulose part of the wood, or lignin, dissolved by the cooking liquor. Some sodium sulphate is added to the black ash (whence the name of the process) to make up losses of alkali, partly through flue gases, and the ash burnt in a furnace till free of organic matter. The smelt is dissolved, forming *"green liquor"* which is causticised by the addition of lime. The precipitated calcium carbonate can either be reburnt or else used on the land. The supernatant "white liquor" is the regenerated cooking liquor. Theoretically the whole of the alkali and alkali sulphide, except flue losses, is recovered and the whole of the non-cellulose part of the wood is burnt up. From a practical point of view, however, although alkali recovery is the essential economic feature of the process, complete recovery is not economically profitable. Although the concentrated black liquor can be economically evaporated down, dried and burnt and the alkali recovered, it is not economic to evaporate the large volume of the more dilute wash liquor, and consequently the effluent will contain alkali salts, dissolved organic matter and suspended organic matter including fibre lost in washing. Since the price of sodium sulphate will be greater in New Zealand than in Europe or America, it follows that it should be economically possible to achieve greater recovery of alkali here than in Europe or America, where the sodium sulphate is manufactured.

In the earlier days of the wood pulp industry in America, no attention was paid to effluent, with the result that in the State of Wisconsin where many mills are situated the rivers became polluted in places to such an extent that fish life was entirely destroyed. The rivers were regarded as Nature's sewers. The seriousness of the situation was revealed by a joint investigation on stream pollution in the State of Wisconsin by the Conservation Commission and the State Board of Health who published a long report in 1927. In this year a permanent State Committee, consisting of the State Chief Engineer, a member of the Railroad Commission, a member of the Conservation Commission and the State Health Officer was appointed. A progress report of the Committee in 1931 showed that marked improvement was being effected and that the industries of Wisconsin had spent nearly 1½ million dollars for equipment or research to recover or treat wastes causing objectionable stream pollution. According to the report "definite methods have been developed for utilisation or treatment and disposal of certain types of wastes produced by (1) pulp and paper mills, (2) canneries, and (3) milk product plants. Use is now being made of these methods in securing the satisfactory solution of existing pollution problems."

Recent records show that marked improvement has been effected in the effluent from Sulphate or Kraft Pulp Mills, the biochemical oxygen demand being reduced to somewhere in the neighbourhood of 100 persons per ton per day of pulp. A hundred ton per day plant might thus be expected to have effluent equivalent to the domestic sewage from a town of 10,000 or less. In one Kraft Pulp Mill in 1932 the population equivalent was down to 20.3, a very low value compared with 1500 for the average sulphite mill.

The question of the establishment of pulp mills in New Zealand has already arisen and a ground wood pulp mill is shortly to be erected at Whakatane. It may be considered desirable on economic grounds to establish in other places mills to produce pulp and paper by one of the chemical processes. With the economic aspect of the problem we are not here concerned, but it is vitally important to investigate in advance as fully as possible any dangers or disadvantages likely to be associated with such a project. Pollution of the air and of streams are two dangers that require careful consideration. When economic advantages outweigh other considerations pollution is by no means an insuperable barrier as is evidenced by the fact that there are more than three hundred pulp mills in the United States and Canada, 86 per cent. of which are situated inland or on inland waterways. The existence of the large planted pine forests in the Rotorua district and the Waikato Valley raises the question of pulp mills inland, and it is important to consider any adverse effects to be expected from the establishment of a pulp mill, for example in the upper part of the Waikato Valley.

Numerous analyses have been made of the water of the Waikato River at various places. The analyses given in Table (I) compiled from published reports of the Dominion Laboratory show that the towns and boroughs of the Waikato Valley have remarkably little effect on the water of the river. There is no detectable increase in the total solids dissolved or suspended in the water, the mean value being 137 parts per million.

TABLE I.

Analyses of Waikato River Water (1924-1933).
In Parts per 100,000.

		Chlorine in Chlorides.	Nitrogen in Nitrates	Ammoniacal Nitrogen.	Albumenoid Nitrogen.	Oxygen absorbed in 4 hrs. at 80° F.	Total Solids.
Arapuni	(1)	1.7	nil.	0.0008	0.0026	0.036	13.0
	(2)	1.65	,,	0.0035	0.0050	0.058	14.0
	(3)	1.5	,,	0.0014	0.0028	0.038	15.0
Hamilton	(1)	2.1	0.005	0.0008	0.0017	0.042	14.5
	(2)	2.1	0.005	0.0008	0.0019	0.040	13.5
	(3)	1.65	nil.	0.0005	0.0020	0.057	13.0
	(4)	1.45	,,	0.0003	0.0022	0.050	12.5
Ngaruawahia		1.9	,,	0.0032	0.0026	0.101	14.0
Huntly	(1)	1.55	,,	0.0021	0.0164	0.346	14.5
	(2)	1.5	,,	0.0010	0.0030	0.085	13.0
Mercer		1.5	,,	0.0008	0.0047	0.135	14.5

The nitrogen in nitrites was in every case nil. The deposits (included in total solids) varied from "medium" to "very large" and consisted of organic matter, silicious particles, diatoms, etc. From the very small effect of borough sewage and the known population equivalent of pulp mill effluent, it can be immediately seen that a large pulp mill would have very little effect on the water of the river. This, of course, is due to the large volume of water. The flow has been accurately measured at Arapuni and found to be

5,000 cusecs (cubic feet per second) at minimum flow. It is interesting to note that at Arapuni the river is normally carrying to the sea some 2,000 tons per day of total solids, mainly in the form of dissolved salts.

From the analyses of the effluent of pulp mills in Wisconsin, it is possible to calculate with considerable accuracy the pollution to be expected in the Waikato River from either a Sulphite Mill or a Sulphate (Kraft) Mill. From the collected data it is evident that there are enormous differences in the efficiency of different mills of the same type. Averages consequently do not give a satisfactory indication of the results likely to be obtained from a modern mill efficiently controlled.

In Table (II) are given data of the effluent from a combined Kraft Pulp and Paper Mill in the State of Wisconsin. The quantities were calculated from the monthly averages for May, June and July, 1935, worked out from the daily analyses (received by private communication). The mill, during the period, produced an average of 57.0 tons of pulp and 66.4 tons of paper or total product of 123.4 tons per day. In the first column are given the analyses of the effluent per ton of total product, and in the second column the pollution that would be caused in the Waikato River at minimum flow by a plant producing 100 tons of product per day of 24 hours.

TABLE II.

Effluent from a 100-ton Kraft Pulp and Paper Mill.

Constituents.	Amounts per ton of products.	Parts per 100,000 in the Waikato River.
Volume of effluent	4747 c. ft.	—
Total solids	234.3 lbs.	0.087
Suspended solids	57.7 „	0.021
Total organic matter	117 „	0.043
Fibre	26 „	0.016
Alkali as Na_2SO_4	156 „	0.058
Aluminium as $Al_2(SO_4)_3$	3 „	0.001

The total solids added to the Waikato River water which normally contains about 130 to 140 parts per million would be less than one part per million, an entirely negligible increase. From the point of view of effect on fish life, the biochemical oxygen demand and the toxicity of any constituents of the effluent must be considered. It has been suggested that for the average mill a dilution of the actual effluent to 1 in 200 is necessary to prevent adverse effects on fish life. Since the actual dilution in the Waikato River would be about 1 in 1000, no effect on fish life should be detectable. If, however, the mill were situated on a small tributary stream, fish life would be destroyed in this stream. The possibility of the fibre in the effluent gradually forming deposits must also be considered. The amount would be about a ton per day, a very small amount compared with the large volume of water, and would probably be undetectable. There is, however, another disadvantage of Kraft

Pulp Mills not taken into account in analyses of effluent, namely, the objectionable smell, which is detectable for miles around. This smell is due to traces of organic sulphur compounds, chiefly mercaptans, dimethyl sulphide and similar compounds. Some of the odoriferous gases are present also in the wash liquors and are evolved on agitation. The toxic properties of the effluent, unless sufficiently diluted, are due chiefly to mercaptans. Our olfactory organs are extremely sensitive to mercaptans and amounts indetectable by chemical analysis may be objectionable. On account of this odoriferous characteristic, aesthetically so objectionable, no sulphate pulp mill should be erected too near any town.

It would appear from the above considerations that a modern Kraft Pulp and Paper Mill efficiently controlled and suitably situated would have very little effect on the Waikato River. Certainly not nearly enough to affect fish life. On the other hand, it is clear that the potential dangers and disadvantages associated with the establishment of pulp mills calls for the greatest caution and the fullest possible investigation before any pulp mill is erected.

Similar caution and investigation are necessary in the case of other industries, dairying, cheese-making, canning, meat works, fertiliser works, gas works, etc. Manufacturing industries are bound to develop in New Zealand with increase of population, and the country will progressively become relatively less dependent on primary industries, and relatively more industrialised. Moreover, industial development cannot be confined to the seaports. Part of the price to be paid for development of manufacturing industries will be the damage to our streams, our clear air, our harbours and estuaries, and it is incumbent on chemists, who alone are in the position to understand and to anticipate such dangers associated with manufacturing industries, to keep the problem continually in view and possibly to urge the Government to establish a permanent Committee to collect information and to advise the Government on this aspect of industrial development.

Industry should be aided, not hampered by such a Committee, which, in this early stage of industrial development in this Dominion, would have a unique opportunity of minimising, if not entirely avoiding those defects and nuisances so frequently associated with manufacturing industries.

SURFACE CHEMISTRY OF PIGMENTS AND PAINTS.

WM. KRUMBHAAR.*

It is surprising how surface chemistry of to-day is more and more revealing a new molecular world, that is to say, the world of the interfacial phase or of the boundary surface layers between solid, liquid and gaseous substances. As experience shows, intermediate layers are unimolecular in many cases, or in other words, they consist of only one layer of single molecules. The thickness dimension of a molecule is negligible compared to the latitude of the surface layer and, therefore, the surface world is not three-dimensional, as our ordinary world, but strange to say, is only two-dimensional. This peculiar condition accounts for the many unique and unusual properties and reactions of the surface systems.

In the line of surface coatings we are especially concerned with the solid-gas phase with regard to pigments and the solid-liquid phase with regard to paints, and in this latter case, i.e., if pigment meets vehicle, surface characteristics are more important than chemical composition. Views of surface chemistry have gained great practical importance for paint making since synthetic resins are coming into use more and more. The surface forces acting in the two-dimensional inter-facial phases are extremely strong, running into hundreds of thousands of pounds per square inch and create physical and chemical conditions within the boundary layer which are completely different from ordinary conditions in the three-dimensional world.

EMULSIONS.

The same holds true for the liquid-liquid systems, in other words for the emulsions which also interest the paint and varnish man. There is a definite trend to-day to produce water emulsions of synthetic plastic resins or synthetic oils which are suitable as paint vehicles. They represent emulsions of the resinous or oily phase in water, so to speak paint vehicles, in which the water takes the place of the volatile solvent.

By cooling emulsions down to sub-zero temperatures the water is frozen out and the emulsion broken up. Moderate cooling below the freezing point as a rule is not detrimental. When the emulsion is spread out on a surface and the water has evaporated the dispersed phase of oil or semi-liquid resin dries to a coherent and homogeneous surface coating film. The drying of such films does not consist merely in the oxidation of the resin-oil phase, but is essentially due to the fact that casein and soaps present become water insoluble. This conversion process needs considerable time, as a whole, several days,

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*Dr. Wm. Krumbhaar, who is Vice-President in charge of Technical Development in Beck, Koller & Co., Inc., Detroit, U.S.A., visited New Zealand in May of this year and kindly contributed this article.

and therefore water emulsion paints will not stand washing with water shortly after application and drying.

Emulsions of the oil in water type stand without decomposition further additions of water and admixture of pigments, provided the pigment has been water wetted beforehand. In order to warrant perfect water wetting the pigment should be treated with a weak casein solution. Interesting problems are involved in the mixing of resin and lacquer emulsions.

The orthodox way to emulsify synthetic plastics or oils is to beat and heat them with weak aqueous ammonia. A small amount of a fatty acid ammonia soap is formed which acts as the ideal emulsifier. The molecules of these soaps are water attractive at the end where the ammonia residue is attached, and they are water repellent at the other end with its long aliphatic chain. In bringing into effect the emulsification, the soap molecules probably orientate themselves in the inter-facial layer with the ammonia end directed to the water and the fatty end turned to the oil and this peculiar orientation explains the good efficiency of ammonia and similar soaps as emulsifiers.

The reciprocal emulsion systems of water dispersed in the oily or resinous phase are of a different character, because they contain the water in a somewhat disguised and hidden form and paints made on this basis resemble in appearance ordinary oil paints. This is the type of water paint that has caused numerous complaints.

If soaps of the type mentioned, are present in varnish materials, even air may be emulsified, though in the ordinary way air does not form stable emulsions in paints. On drying, the air is liberated in the form of bubbles, which may cause pinholing defects and other irregularities of the dried surface film.

ACTIVITIES ON PIGMENT SURFACES.

As mentioned before, the advent of the synthetic resins has created a number of new problems in the field of paint and enamel making, many of which are problems of surface chemistry. They deal with the forces acting on pigment surfaces, with the vehicle envelope formed around the pigment particles and are concerned with pigment-vehicle relations generally.

Surface Conditions:

In order to have a clear understanding of the surface activities of pigments especially with synthetic resins, it is necessary to realise that three different types of surface actions are possible. The first type is the reaction of basic pigments with free acids forming regular soaps.

The second type of surface activities is shown by so-called inert pigments, such as lithopone. Although such pigments are not capable of entering into true chemical reaction, semi-chemical processes which are not soap formation take place nevertheless at the boundary between pigment and vehicle.

The third and most important type of surface activities is due to the special surface forces of adsorption. Certain pigments such as prussian blue, carbon black display especially high adsorption activities. In all cases adsorption leads to the formation of a coherent surface layer around the pigment particle acting as a protective envelope.

The surface forces and activities of dry pigments are governed by the properties of the particle surface. This means in case of pigments with layer structure that the substance and the condition of the outer layer is deciding, while the nature of the inner nucleus is immaterial. This is true for example for extended titanium pigments, which contain the barium-or calcium sulphate in a shell of precipitated titanium dioxide. It also holds true for lithopone. As is generally known, lithopone consists of barium sulphate particles with a coating of zinc sulphide, the outer layer probably being uneven and only covering the inner core as to 75%. Layer structure also influences the behaviour of colour lakes, which are characterised by a layer of dye-stuff deposited upon the surface of a substrate.

Physical surface conditions of pigments vary according to the shape and size of the primary particles and according to the type and degree of agglomeration. All commercial powdered pigments are aggregates composed of closely packed individual particles, which enclose between themselves more or less large cavities of different shape. If these microscopic vacuoles are numerous and empty they produce micro-porosity of the surface of the aggregates. If they are filled with the dry residue of aqueous salt solutions, the particles may be cemented together causing grittiness of the pigment. Many other variations of surface conditions are possible due to the different production methods of pigments.

Pigment Grinding:

The object of paint grinding is the breaking up of the agglomerates. This is done either by the pressure and the friction of hard surfaces on the pigment in the usual paint grinding machinery or is effected solely by the shearing forces of the vehicle, without any direct pressure or friction, as is the case in the disperser type mixers. The higher the viscosity of the vehicle the better the dispersion effect. By actual microscopic counting of dispersed particles in an apparatus as used for counting blood corpuscles it can be shown that, for instance, a bodied linseed oil has a dispersing power of the order of about ten times as high as that of a thin linseed oil.

Roller mill grinding, appreciated in our trade for decades, actually combines the effect of the friction of hard surfaces and the action of the shearing forces within high viscosity vehicles and, therefore, in a way, may be considered as the ideal method of breaking up particle agglomerates.

As far as synthetic resin paint vehicles are concerned, most of the short and medium length type alkyds have to be applied in thin solutions, because when used as highly viscous grinding media, livering may occur. Generally speaking, long oil alkyds are safe and, therefore, by using them, it is possible to take advantage of the merits of high viscosity vehicles for pigment dispersion in disperser type mixers or on roller mills.

The grinding effect on pigment aggregates is especially pronounced, if the primary individual particles are very small, as for instance in the case of pigment dye-stuffs, which are insoluble salts of dye-stuffs. In this case dispersion may lead to a product which, in thin layers, appears transparent as if the pigment were dissolved in the vehicle.

Gaseous Envelopes:

Dry pigment particles are covered with a thin film of air. The surface forces attracting the gaseous envelope are so strong that sometimes even the application of vacuum would not remove the air. Ordinarily, of course, the air envelope is removed by the grinding operation. It seems as if the air film is more efficiently eliminated by the shearing forces, developed by the interior strain of high viscosity vehicles than by the pressure and friction of the grinding surfaces in the usual machinery.

Sometimes the air envelope is only partially removed, as for instance, with bronzing pigments. In this case the partially wetted pigment particle is floating on top of the vehicle, the perfectly wetted part of its surface being in direct contact with the liquid, while the part still covered with a residual air layer turns to the outside. It is probable, that the leafing properties of aluminium powder are governed by similar surface conditions and that the so-called flooding or flotation of pigments is based on similar wetting phenomena. At least it has been shown experimentally that by enveloping pigments with certain perfectly wetting organic substances, such as methyl cellulose, flooding can be decreased considerably.

Just as air films envelope pigments, water films sometimes form envelopes around the particle surfaces and cause technical difficulties because the water layer, activated by surface forces, leads to partial hydrolysis of the vehicle if ground with the wet pigment. As a rule water films are difficult to remove. They are not eliminated by the ordinary grinding operation unless heat and vacuum are applied.

Protective Envelopes:

Many of the difficulties caused by both air and water films can be overcome by enveloping the dry pigment with a layer of substances, that are attracted by the surface forces and satiate them. As a rule, very small amounts of such substances will suffice. Experience shows that an adsorbed envelope of the thickness of a monomolecular layer provides sufficient protection.

Most suitable for these purposes are fatty acids, for instance, linseed oil fatty acids. Contrary to the corresponding glycerides they form very stable envelopes around the pigment. The fatty acid orientates itself in the layer, the carboxyl group being attached to the pigment surface. The orientated layer acts as a lubricant. It prevents the particles from sticking together, enables their free movement relative to each other and thereby improves the dispersing effect.

Systematic investigation shows that the dispersing efficiency of fatty acids increases with the chain length, but only up to 12-14 carbon atoms, corresponding for instance to lauric acid.

It should be mentioned, however, that not every dispersion is connected with the formation of orientated layers. For instance, certain low molecular organic acids, such as malic acid, are excellent anti-settling agents, the practical procedure being to dissolve ½ to 2% of this material in the paint vehicle. A very good dispersing effect is also displayed by neutral polymerised oils, if sufficient mechanical force is applied to thoroughly wet the pigment.

Certain soaps also provide effective envelopes, as for instance, aluminium stearate and it seems as if the so-called stearated pigments will gain some practical importance. Another method uses barium resinate, which is attracted firmly, satiating the adsorptive capacity of the pigment. Zinc naphthenate is also supposed to form a monomolecular layer around the pigment particles.

In order to cover the pigments with the thin layer, they are usually treated with very thin solutions of the soaps in a volatile solvent. These and other similar possibilities so far have not been exploited sufficiently. It is known that the adsorption of cobalt compounds by white pigments can be inhibited by zinc soaps, but without any doubt there are many other possibilities of decreasing by similar means the drier adsorption exerted by pigments which quite often leads to serious decrease and even complete loss of the drying in enamels and paints.

SURFACE ACTIVITIES IN PAINTS.

Vehicle Envelopes:

While the protective envelopes on dry pigments do not, as a rule possess more than unimolecular thickness, the envelopes formed around the particles, if a pigment is ground into a paint vehicle, are considerably thicker. In paints and enamels the vehicle itself is adsorbed and not the volatile solvent. Therefore, studies of adsorption in straight solvents or solvent-mixtures, as for instance those that are based on sedimentation volumes have no bearing on the behaviour of the envelopes around pigments in actual paints and enamels.

In these cases the vehicle is linked to the pigment surface by the adsorption of those components that respond most easily to the surface attraction and form the most stable envelopes. As a rule fatty and resinous acids are most responsive to adsorption forces, and, therefore, a certain amount of acidity is desirable in paint vehicles. In view of the power of the acting surface forces it is probable that multimolecular layers of the vehicle are surrounding the first envelope of acidic material which is in direct contact with the particle surface.

In applying several different vehicles after each other, it has been found that the layer on pigments, formed primarily, will be held tenaciously, will not be displaced by other substances present in the vehicles added afterwards, and will be maintained, even when the paint is diluted with strong thinners. These points are of great practical importance and explain why occasionally the sequence of addition affects the quality of the paint product. As a rule the first vehicle should be of the non-reactive type, followed by the more reactive sort, for instance, in producing alkyd resin enamels the actual grinding should be done with the long alkyds and the short oil resins should be added later on.

The envelope adsorbed from the vehicle is able to effect a very good protection of the pigment in the dried film, provided the vehicle itself has good resistance. A vehicle that in itself is alkali fast, will protect the pigment against the action of the alkali. If it is light resistant it will suppress influences that cause fading of the pigment. If it has good weathering properties it will reduce chalking to a certain extent.

Pigment-Vehicle Reactions:

The close contact between pigment and vehicle on the other hand leads to many more or less desirable reactions in paints and enamels. The degree of dispersion influences largely the reactivity. As a rule, of course, dispersion should be as perfect as possible. But if dispersed too far, pigments, otherwise inert, may become reactive thus producing the phenomenon of over grinding. This sometimes happens with titanium dioxide and certain synthetic vehicles resulting in a seedy looking surface film. In some cases only a limited break up of agglomerates may be necessary in order to produce a particle size best suited for creating thixotropy.

Flocculating and settling are some of the troublesome reactions that are often blamed on synthetic vehicles. They are due to the types of reactivities mentioned beforehand, that is to say, due to chemical, semi-chemical and mostly surface forces. In some exceptional cases the formation of pigment flocculates and sediments may be due to static electricity. By the friction of the grinding operation the particles may take opposite electrical charges, may hold these charges in the oily medium and then may attract each other to form aggregates, which cause seeding and settling. Dispersing agents like fatty acids or conducting pigments like carbon black and aluminium, however, inhibit electrification completely.

Flocculation and sedimentation may be reduced by additions of substances mentioned before which form protective envelopes around the pigment particles. Among these agents blown oil seems to be especially efficient.

Livering and gelation are two other phenomena often observed in paints and enamels and especially in those with synthetic alkyd resin vehicles. They are caused by the peculiar condition of many alkyd resin solutions which seem to be in a state of suspended gelation. By the surface action of the pigment the gelation is gradually carried on, increasing first the viscosity and rigidity of the paint and finally leading to a gel. These difficulties may be overcome to a certain extent by adding to the paints and enamels, dispersing agents, which satiate the surface forces of the pigments. The difficulties may be furthermore reduced by choosing synthetic resin solutions of higher stability.

Pigment vehicle reactions not only take place in the liquid suspensions present as paint or enamel in the container, but also in the film after drying. They consist mostly of soap formation, which helps in reinforcing the film.

Thixotropy:

For some purposes, as for instance in flat wall paints, a certain type and degree of reactivity between pigment and vehicle is desirable, producing the viscosity and flow properties known as thixotropic. Thixotropy means in plain English " change by touch," in other words, the tendency of a paint to become more free flowing on stirring, shaking or brushing. It is different from false body which is characterised by high viscosity with relatively low content of non-volatile. Of course there exist a number of types which are intermediate in properties between the two extremes of false body and thixotropy.

Thixotropy is the important property that imparts easy brushability to otherwise viscous paints and enamels and that prevents sagging and other irregularities of finishes, such as curtains when applied to vertical surfaces. Although there is much theoretical information available on thixotropy, no practical rules have been established so far with regard to the influence of pigment and vehicle characteristics on thixotropy. It is known, however, that certain types of alkyd resins impart thixotropy to paints.

THE REQUIREMENTS OF A HIGH-SPEED DIESEL FUEL.

M. L. STEWART.

In considering the properties of fuel for Diesel engines, it is essential that one should be familiar with the engine itself, but to give, even in outline, the different types into which the "Diesel" engine can be subdivided would require more space than is available. This paper will therefore deal mainly with the fuel characteristics as required by the modern High-speed C.I. Engine.

Combustion in the High-speed Compression Ignition Engine is similar in many respects to combustion in the spark ignition gasoline engine, in fact the combustion cycle necessary for high-speed operation is intermediate between the constant volume (Otto) cycle of the gasoline engine and the true constant pressure cycle patented many years ago by Dr. Diesel.

In the gasoline engine all the fuel and air are taken into the chamber or cylinder during the suction stroke already thoroughly mixed. This homogeneous mixture is compressed and shortly before top dead centre (5°) the charge is ignited by means of an electrical spark. From the time the inlet valve opens to the point at which the fuel ignites there is approximately 360° of crank angle in which to prepare the fuel for combustion.

i.e. 1/50th sec. at 3,000 revs.
1/40th " " 2,400 "

In the Diesel engine, however, air only is taken into the cylinder during the suction stroke—air only, is compressed. The fuel is injected shortly before the end of the compression stroke (approximately 5°C. before T.D.C.) and is ignited by the heat of compression. Injection, penetration and intermixing take place within approximately 30°. Just what this means can be the more readily appreciated if it is realised that it is required to both meter and inject in an atomised form a quantity of fuel of the order of .001 cubic inch in 1/500 seconds (at 3000 revs.). The development of a suitable pump, by the Bosch Comp. some few years ago, in itself no mean achievement, gave the High-speed C.I. Engine a decided impetus.

DIESEL FUELS.

Usual Laboratory Tests:

Some idea of the requirements of Diesel fuel may be obtained by a consideration of the usual laboratory routine examination.

Specific Gravity:

No direct indication of fuel suitability, but it is useful for calculating fuel consumption. A high specific gravity means a high calorific value in B. Th. U's per gallon—hence a smaller volume of fuel for given power output.

Viscosity:

As a general rule, the C.I. Engine requires a light fuel of viscosity about 35/40 sec. R.I. at 100°F. Should the figure exceed these values to any extent, trouble may be experienced with atomiser nozzles; also careful experimental work has determined that the viscosity must be kept below a maximum in order that a fine dispersion may be obtained. Too low a viscosity may lead to too fine a degree of atomisation with consequent loss in penetration of the fuel into the combustion chamber. The lower limit is also set by the need for lubrication and too low a viscosity leads to leaking at the pump with consequent loss of fuel.

Distillation:

This is carried out in a manner somewhat similar to that used for motor spirits—its value is mainly confined to the identification of a fuel and for purposes of standardisation. As will be shown later, generally speaking, the C.I. Engine requires a distillate, although instances are on record where pressure distillate bottoms from the re-running of cracking still distillates have functioned satisfactorily in Diesel Engines of certain types. For slow-running Diesel Engines, blends of distillates with residual oils and even-preheated residual oils themselves have been used successfully.

Sulphur:

There is no direct evidence that sulphur is harmful within reasonable limits. (Some fuels contain up to 4%).

Asphaltenes:

This need be considered only in the case of high viscosity grades, especially those containing residual oils. An asphaltene content of less than 0.3% can usually be taken to indicate a distillate.

Pour Point:

This is important—the pour point should not be above the lowest temperature at which the fuel is to be used. In almost every fuel a waxy precipitate occurs at temperatures above the pour point and considerable work has been carried out by the Shell Laboratories to evolve a method by which this wax separation can be observed. The method in outline consists in decolourising the oil with a decolouring agent either directly or after suitable treatment and then determining the cloud point on the clear filtrate. This control is employed on all supplies of Diesel Fuel Oil obtained by the Company in New Zealand. The precipitation of wax is a serious matter, since it would gradually block the filters and interfere with the fuel supply.

Flash Point:

This has no effect on the behaviour of a fuel in a Diesel or High-speed C.I. Engine.

Calorific Value:

Controls consumption. There is little variation in petroleum fuels (18,500/19,500 B.Th.U.'s per lb. fuel).

Ash:

Usually below 0.01%. Indicates the extent of mineral impurities. Grit, sand, etc., should be absent, since they tend to choke the filter and, should any reach the fuel pumps, would cause serious wear of both pump and injector nozzles.

Water:

Usually less than 0.10%. Settles out readily. B.E.S.A. Specification "A" for heavy Diesel Engine allow up to 0.05%.

COMBUSTION.

In the *petrol engine* the combustion can be considered as taking place in two stages.

Stage 1.—The delay period during which the flame nucleus is developed without any perceptible pressure rise. This period between the passage of the spark and the beginning of the rapid pressure rise is governed by—

(a) Chemical nature of the fuel.
(b) Mixture strength.
(c) Temperature and pressure of the charge.
(d) Degree of turbulence.

Stage 2.—The period of rapid pressure rise during which the flame is spread throughout the combustion chamber. The rate of pressure rise, which governs the knocking (detonation) characteristics of the engine depend on—

(a) Size and shape of combustion chamber.
(b) Degree of turbulence.
(c) Chemical nature of the fuel.

Ricardo was the first investigator to analyse the nature of combustion in the *High-speed Diesel Engine* and found that it may be considered as taking place in three distinct phases.

Stage 1.—The delay period during which part of the fuel is injected and this flame nucleus developed without any appreciable rise in pressure. It is suggested by Ricardo that "ignition first starts from some nucleus point as soon as a minute portion of the injected fuel has had time to vaporise and to mix with sufficient oxygen to form a readily combustible mixture and that from this nucleus the flame spreads in much the same manner as in the spark ignition petrol engine during the first phase." This period of time between the beginning of injection and the beginning of rapid pressure rise, depends on—

(a) Chemical nature of the fuel.
(b) Temperature and pressure of the air at the time of injection.
(c) Volatility.
(d) Rate of injection.
(e) Degree of atomization.
(f) Degree of turbulence.

Stage 2.—The period of rapid pressure rise in which the quantity of unburnt fuel already injected during the delay period ignites at a rate practically uncontrolled by—

(1) Combustion chamber design.
(2) Degree of turbulence.

and in a small way perhaps by

(3) The chemical nature of the fuel itself.

Part of the fuel charge is also injected during this phase, but its effect on the rate of pressure rise is relatively small. As in the gasoline engine, combustion shock in the Diesel Engine is related to the rate of pressure rise, i.e., the greater the rate of pressure rise the greater the engine roughness.

Stage 3.—The period of almost constant pressure during which the fuel burns substantially as it is injected. By controlling the rate of injection this pressure can be varied either to bring about a further rise in pressure or to maintain constant pressure.

In the petrol engine combustion proceeds relatively slowly at first and very rapidly at the end. The "knock," if any, may be said to be due to the last portions of the fuel to be burnt. In the Diesel Engine the fuel does not ignite immediately after the commencement of its injection, but only after a certain delay when the whole quantity of the injected fuel then available will ignite almost simultaneously, thus causing the " knock."

It has been definitely shown that the rough running of a Diesel Engine is closely associated with this delay period. Further, it has been demonstrated that this period consists of a physical and a chemical delay. The physical delay is largely governed by the heating and evaporation of the injected fuel droplets. The chemical delay occurs during the development of heat from the reaction of the vapours formed during the physical delay until flame temperature is attained when Stage (2) commences. Actually the two delay periods overlap. For normal light Diesel fuels the chemical character governs the total ignition period showing that the physical delay is relatively short. This is due to the increased volatility of such fuels as compared with residuals.

Of the six factors controlling the delay period—the first and third, chemical nature of the fuel and volatility, are the chemist's particular concern. The other four are engineering problems and the concern of the designer. The degree of atomization perhaps requires the attention of the chemist but the factors controlling this are for the most part fairly well understood.

No purely chemical method has yet been devised whereby such a complex mixture as a petroleum Diesel fuel can be examined with sufficient accuracy to enable its behaviour in the engine to be predicted and therefore engine behaviour is the deciding test.

Various methods have been proposed for the evaluation of the ignition quality of fuels and most of these methods are based on—

1. Spontaneous ignition temperature.
2. Delay angle measurement.
3. Critical compression ratio.

1. The spontaneous ignition temperature is the lowest temperature at which the fuel surrounded with oxygen in a bomb will ignite without the application of a spark. It is often referred to as the Self Ignition Temperature or Ignition Point, and has no connection with either Flash Point or Fire Point as commonly understood. Difficulties have arisen in the use of the S.I.T. method since some fuels like petrols have been found to give higher values than those obtained on heavier distillates, while several workers find no general relationship between S.I. Temperatures and engine performance.

2. Delay Angle Method.—This method was developed by Boerlage & Broeze[1] in the Shell Company's laboratories and results represent the angle the crankshaft travels from the time the fuel is injected until it ignites. Boerlage & Broeze used a 20 h.p. single-cylinder Thomassen Engine running at 450 lbs./sq. in. pressure and obtained their results by means of optical diagrams.

3. The critical compression ratio method was developed by Pope & Murdock[2] in America. They used a modified C.F.R. Engine, driving it by means of an electric motor and varying the compressed pressure until audible combustion occurred.

In both the Delay Angle Method and The Critical Compression Ratio Method the results are subject to engine and atmospheric variables. To overcome this a standard reference fuel such as the iso-octane/heptane standard for petrols has been tried. Cetene and mesitylene were tried at first but Boerlage & Broeze have advocated the use of α-methyl-naphthalene as the " poor " fuel, and their results are given in cetene numbers, i.e., the percentage of cetene blended with α-methyl-naphthalene which matches in delay angle the fuel under test.

Stansfield has recommended that critical compression ratios be also given in terms of cetene/ α-methyl-napthalene blends. He finds good agreement between delay angle values and those obtained by the starting test (a form of critical compression ratio) except in the case of "temperature sensitive" fuels or doped fuels.

From recent work in England and Europe indications are that a laboratory test method, in which delay angles are measured in a regularly running engine, is preferable to measurement of critical compression ratios in a motored engine.

Recently Boerlage & Broeze[3] have shown that there is an optimum value for the ignition quality of Diesel fuels. This optimum varies with different types of engines and arises from the fact that with very early burning fuels, the combustion being near the nozzle obstructs the oxygen from reaching the latter part of the charge.

From the consideration of the double nature of the delay period, it is evident that both volatility and cetene value determine this optimum ignition value.

Dopes:

The use of dopes (such as have been used for petrol) have been suggested and tried. It will, of course, be obvious that the requirements of a good Diesel fuel are the reverse to those of a good motor spirit, and in the same way a suitable dope for a Diesel fuel would be a pro knock dope for petrol. Among those tried are the following—

Amyl nitrate
Ethyl nitrate } too expensive
Benzaldehyde—decomposes too rapidly
Acetaldehyde—too volatile.

From the foregoing, it will be seen that the Diesel Engine, and especially the High-speed C.I. Engine, does not possess the omnivorous appetite commonly supposed. It is of course desirable that the Diesel should work over as wide a range of fuels as possible.

To the chemist falls the task of providing the correct fuel, and of improving poor fuels so that they are at least usable.

A close study of the chemical characteristics affecting "ignition delay" is necessary. A readily crackable oil is a better Diesel fuel than one which is more stable. Furthermore, a preliminary cracking of a fuel lowers its ignition qualities in direct proportion to the severity of the cracking conditions.

Boerlage & Broeze suggest that thermal stability is dependant on molecular structure and in general the more compact the molecule the higher the thermal stability—hence aromatic rings are more stable than paraffinic chains:—

e.g.	Paraffin Wax	Benzol
	Cetene (C_{16} H_{32})	Tetra iso-butylene ($C_{16}H_{32}$)
	(Straight Chain hydrocarbons)	(Branched Chain)

Thus paraffin wax is easy to ignite and difficult to burn, while benzol is difficult to ignite and easy to burn once it is ignited.

The following table given an approximate comparison of Critical Compression Ratio and Cetene Numbers:—

Critical Compression Ratio.	Cetene No.	Remarks.
7	100	Diesel fuels which operate well in the average engine.
8	58	
9	45	
10	40	Gasoline from 50/70 octane falls in the class. Diesel fuels give trouble in all High-speed Diesel Engines. Good for spark ignition-injection engines.
11	35	
12	30	
14	22	Impossible to use in Standard Diesel Engine. Tar oils fall in this class—require supplementary ignition fuel.
16	15	
20	0	

In conclusion, the writer desires to express his thanks to the management of The Shell Company, New Zealand, Limited, for permission to refer to research work carried out in the Company's Laboratories.

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THE OCCURRENCE OF LACTOFLAVINE IN BYPRODUCTS FROM LACTOSE MANUFACTURE.

W. G. WHITTLESTON.

Some preliminary work was done on the stability of lactoflavine solutions, and on methods of evaporation at low temperatures; it is, however, only necessary here to describe the final methods adopted in the work done.

In preparing concentrates of the required material, the process divides itself into four main sections:—

1. The extraction of pigment—a process which results in large amounts of impurities being also extracted.
2. The concentration of the extract at a low temperature.
3. Purification of the solution by (a) adsorption, or (b) elution.

Preparation of Lactoflavine Concentrates from Whey-paste.

1. The method found most satisfactory for the extraction of whey-paste was as follows:—

Four hundred and fifty g. of whey-paste was placed in a round-bottom flask, together with 750 ml. of rectified spirits. The whole was boiled for 2-3 hours over a water bath, carbon dioxide being led into the flask by a tube which opened near the surface of the liquid, thus keeping the boiling liquid in an atmosphere of inert gas. The contents were vigorously stirred by a small glass propeller stirrer, while the contents of the flask were shielded from light by a tinned iron cylinder surrounding the latter, and covered with a thick card through which the neck of the flask projected. Usually the mixture was allowed to stand overnight, and the next morning the supernatant liquid was decanted off, the remaining sludge being filtered in a Buchner filter, and the filtrate added to the decanted liquid. The extract was then chilled by a mixture of ice and salt, thus throwing out a good deal of lactose from the solution which was again filtered.

The solid residue from the extraction process was re-extracted with a similar amount of alcohol in the same way as above.

2. Concentration of the above extract was carried out in the evaporator described at the end of this paper. The concentrate was chilled as before, and filtered.

3. Fuller's earth was used as the adsorbant in the process of purification. The adsorption was carried out as follows:—

Three hundred and fifty ml. of the concentrate, 500 ml. of 2N hydrochloric acid, 500 ml. distilled water, and 15 g. of fuller's earth were placed in the same apparatus as was used for the first extraction. The mixture was stirred in an atmosphere of carbon dioxide, as before, for 4-6 hours at room temperature. After standing over night, the supernatant liquid was poured off, and the residue treated as before. Filtration was found to be made easier by flocculating the fine clay suspension with enough dilute acetic acid to make the solution just acid to litmus. It was not found worth while to re-elute the fuller's earth residue.

It should be noted that all operations were carried out in subdued light, as the normal light of the room was found to be strong enough to decompose lactoflavine solutions exposed to it for any length of time.

Using a colorimetric method of estimation with a solution of potassium chromate as standard, it was found that the unevaporated extract contained 30 γ/ml. of the pigment. The concentration in the original whey-paste was 21γ/gm.

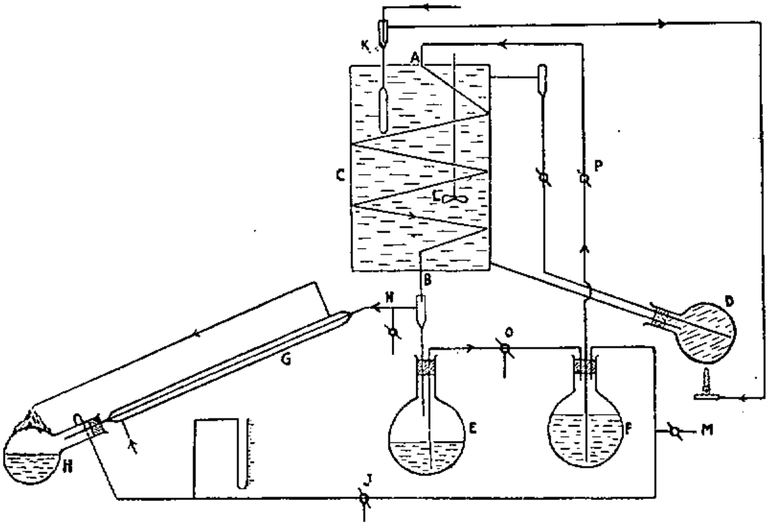
Owing to the fact that the solutions contained coloured impurities, it was necessary to devise a method of estimation using some other property than depth of colour. The strength of fluorescence was used as a rough index of concentration. A solution of the pigment was carefully prepared by several adsorptions and elutions; this was compared with the chromate solution, thus finding its approximate strength. Unknown samples coloured slightly by impurities were compared with the standard flavine solution thus:—

The solution to be tested, and the standard were placed in Nesslerising tubes, and illuminated at right angles to their length. The source of light was a half-watt electric lamp inside a tin box fitted with a pane of cobalt glass, operations being carried out in a dark room. By this means it was found possible to estimate the strengths of solutions in the usual manner.

Some samples of green refined lactose were available which were contaminated with lactoflavine adsorbed on the surface of the crystals. With the object of getting a solution of lactoflavine in a volatile solvent, from which a small quantity of the solid might readily be obtained, the following solvents were tried as a means of removing the pigment from the lactose without dissolving the latter:—Ether, ether-and-alcohol mixture, methyl alcohol, methyl alcohol-and-water, absolute ethyl alcohol, ethyl alcohol and water (1:1). Only the latter was of any use, and it had to be used at a low temperature to prevent the solution of a small quantity of lactose. The amount of flavine on the sugar was estimated to be 5.4γ/gm. of dry sugar.

A quantity of press cake from the filters used in clarifying lactose solutions in the process of manufacture was also available. 125 g.

of this material were eluted with a mixture of 75 ml. pyridine, 75 ml. methyl alcohol, and 250 ml. of water. The operation was carried out in the same apparatus as was used in the elution of fuller's earth. Elution was carried out five times on one sample, and the final eluate was about one half of the strength of the first. The first eluate contained approximately 150 γ/ml.—the highest concentration obtained by elution.



Owing to the undesirable properties of pyridine, attempts were made to find another eluting agent for the press-cake. The first substitute tried was an aqueous alcoholic solution of ammonia. This was found to be quite useless in an atmosphere of carbon dioxide, which it absorbed, so an atmosphere of hydrogen was substituted. The solution, however, still tended to become neutral, and very little elution took place. Dilute sodium hydroxide solutions were tried, and were equally unsuccessful.

An attempt to concentrate the eluate by freezing was made, but owing to the inadequate means available, it was abandoned.

Final Concentration.

The combined eluates from the elution of several batches of press-cake, after chilling and filtering, were evaporated in the evaporator to be described. The concentrated solution was placed, after removal from the evaporator, in a vacuum desiccator for the final removal of solvent. The work had to be discontinued before any solid concentrate could be obtained.

The Evaporator.

The evaporator used in this work is illustrated in the accompanying diagram. AB is a thin-walled glass worm, contained in the outer heating jacket C which is kept at a constant temperature by the thermo-regulator K controlling the burner under the heated flask D. A circulation of warm water is set up in the system, supplying the necessary heat for evaporating the liquid passing down the worm. The liquid to be evaporated is sucked into the flask F via the tap O, a vacuum being applied at J. The vacuum is then turned on to the solvent receiving vessel H by means of the two-way tap at J, M is opened, O is closed, while P is adjusted to give the required flow of solution. The concentration of the solution in E is controlled by the rate of flow of the solution down the worm. If it is required to pass the liquid through the evaporator again, the vacuum is turned on to the flask F, N is opened, P closed, and O put to the straight through position. The cycle may now be repeated.

With this evaporator, it was found possible to remove quite large amounts of solvent in a short time at the low temperature of 22-23°C. It has the advantage that the liquid is not subjected to heat for any long time, and being almost automatic, requires little attention. In order to prevent the lactoflavine solution from being decomposed by light, the glass flasks on the apparatus were enclosed in tins, while the glass tubes through which the solution flowed were painted.

Summary.

1. The lactoflavine content of whey-paste (21 γ/g.) green refined lactose (5.4γ per g.) and press-cake from the filters used in the manufacture of pure lactose, has been found.

2. A low temperature evaporator suitable for evaporating heat-sensitive liquids at temperatures from 22-25°C. has been designed.

The author wishes to thank the trustees of the Lubecki Scholarship which enabled this research to be carried out.

THE MICRO-DETECTION OF COBALT.

T. A. THOMSON and E. M. THOMSON.

In Mikrochemie Band XV, Z. Stary contributed a "Sammelreferat" on "The Micro-estimation of Nickel and Cobalt." In view of the present interest in cobalt it was decided to compile a paper on similar lines. We have included a short section on qualitative work, mentioning the methods we have found satisfactory.

We have used Feigl's phrase "limit of identification" as described by Emich[1], i.e.: Limit of identification = least weight of active ion detectable by a reagent (usually expressed in γ, where $1\gamma =$ one millionth of a gram).

QUALITATIVE ANALYSIS.

(a) *Crystallograhic.*—The three most common reagents are:

1. *Potassium Mercuric Thiocyanate*[2].—Forming $Co(SCN)_2.Hg(SCN)_2$. Limit of identification, 0.0001 γ cobalt.

2. *Potassium Nitrite*[2].—Forming $K_3Co(NO_2)_6.1\frac{1}{2}H_2O$. Limit of identification 0.1 γ cobalt.

3. *Pyridine Hydrochloride and Ammonium Thiocyanate*[2].—Forming $Co(SCN)_2.(C_5H_5N.HSCN)_3$.

Of these (1) is very sensitive; however, the limits of proportion are not satisfactory as Cd : Zn : Co; 1 : 1 : 1 gives only the reaction for zinc.

(2) is sensitive, but the crystals formed are not distinctive, therefore difficult to identify in a mixture, though it must be noted that nickel does not give this reaction.

(3) is unsuitable for routine work as many other ions interfere.

Moreover crystallographic tests, while having good limits of identification are generally poor in limit concentration, i.e., it is frequently more convenient to treat very small volumes at relatively high concentration, than larger volumes at greater dilution.

(b) *"Spot" and Colour Reactions*:

1. *Dithio-oxamide* (*Rubeanic Acid*)[3] in alcoholic solution in the presence of ammonia gives with cobalt, copper, and nickel, amorphous salts.

One drop of the solution which may contain copper, cobalt, and nickel is placed on a paper (previously impregnated with a saturated alcoholic solution of the reagent and dried) and then held over ammonia. If all three metals are present a green spot (copper) surrounded by two circular zones—the inner purple one due to nickel, and the outer yellow-brown one due to cobalt, will be found.

For those who are not familiar with "spot" analysis we recommend the use of tartrate ions to prevent the apparent interference of iron.

With solutions free from copper and nickel the limit of identification is 0.03 γ cobalt, and the limit of concentration is 1/1,660,000.

2. *α-Nitroso β-Naphthol*[3] forms precipitates with ferric, uranyl, tin, silver, chromium, bismuth, copper, palladium, and cobalt salts. (Nickel, lead, manganese, aluminium, calcium, magnesium, potassium and sodium do not interfere). Of these compounds, those formed by cobalt and palladium are specially suitable for analytical use.

To a drop of neutral solution on a paper is added one drop of reagent. An orange-red to brown fleck, stable in dilute sulphuric acid, indicates cobalt.

Limit of identification	0.05 γ cobalt.
Limit of concentration	1/1,000,000

Reagents: 1 gram α-nitroso β-naphthol dissolved in 50 ml. glacial acetic acid and made up to 100 ml. with water; 2 N sulphuric acid.

For the separation of cobalt from ferric iron, ammonium fluoride or sodium phosphate may be used, enabling 0.5 γ cobalt to be detected[4], in the presence of 1,000 times this amount of iron. Copper may be removed by the addition of potassium iodide (sulphite being used to remove the iodine produced).

With a solution of 0.1 gram α-nitroso β-naphthol in 20 ml. of very dilute sodium hydroxide, filtered and made up to 200 ml., Böttger[5] detected 0.006 γ cobalt in a drop of 0.01 ml.

Belluci[6] by the use of β-nitroso α-naphthol detected 0.06γ cobalt/ml.

3. *Nitroso derivative of Sodium β-naphthol disulphonate (Nitroso-R Salt)*[7] produces with cobalt salts, a deep red colour. Although the limit concentration given is only 1/33,000, this reagent is popular, as it can be used in acid solution. Moreover, it separates cobalt from nickel, iron and zinc.

To the test solution is added ½ part of sodium acetate and an equal volume of the reagent; boil. After adding ¼ part of concentrated nitric acid (to destroy the colour produced by iron) and reboiling for one minute, a permanent red colour indicates cobalt.

Reagents: 0.5% aqueous solution of nitroso-R Salt; concentrated nitric acid; solid sodium acetate.

QUANTITATIVE ANALYSIS.

(a) *Gravimetric*:

1. One of the best procedures is to separate cobalt electrolytically and weigh as cobalt. This method has been improved upon recently. Okáč[8] uses a plantinum mesh electrode. When nickel is also present both metals are quantitatively precipitated after about 15 minutes (using micro amounts). The cathodic deposit is then dissolved in nitric acid, the nickel precipitated by diacetyl dioxime; the excess of precipitant is then destroyed by hydrogen peroxide and hydrochloric acid. The cobalt is finally redeposited and weighed.

For these and other micro-electrolytic procedures the Emich electromagnetic micro-balance is more suitable than the normal Kuhlmann type, as weighing down to 0.015γ may be made with greater speed and accuracy than the ordinary machine, which is reliable under these conditions for perhaps 2—5γ.

2. The precipitation of cobalt as oxide is generally followed by a reduction to metal by hydrogen. The standard macro methods are capable of being used on a micro scale.

3. The use of phenyl-thiohydantoic acid[9] does not seem to have met with much favour. Unlike many organic reagents, the compound formed by phenyl-thiohydantoic acid with cobalt is not weighed as such but converted into oxide, and so does not give a great increase in accuracy, though it permits immediate separation from nickel and iron.

(b) *Volumetric*:

Of the few volumetric methods in the literature only the oxalate one has been tried by the authors of this paper. It follows on the normal micro calcium method, the oxalic acid being titrated manganometrically or cerimetrically.

(c) *Colorimetric*:

1. The use of nitroso-R Salt (given above) has been suggested for colorimetric work but, as the lower limit is 0.1 mg., the method is not of the widest application.

2. The reaction of diacetyl dioxime in ammoniacal solution as given by Bertrand and Macheboeuf[10] follows.

Nickel is precipitated with diacetyl dioxime, the filtrate evaporated, heated, and the residue taken up in hydrochloric acid. The alcoholic solution of the reagent and ammonia are then added. The orange colour produced by cobalt is matched as usual. Limit of comparison, 10γ.

In conclusion we wish to acknowledge the help of Hofrat. Prof. F. Emich of Graz for details of the construction and use of his electro-magnetic micro-balance.

Microchemical Bureau,
Waikari, Dunedin.

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ANNUAL CONFERENCE, 1936.

The 1936 joint Conference of the New Zealand Institute of Chemistry and the Institute of Chemistry of Great Britain and Ireland (N.Z. Section) was held at Dunedin on January 29 and 30. Although the attendance at the southern centre was somewhat small, the Conference was highly successful.

The proceedings opened on the evening of January 28, when an informal welcome, with supper, was tendered to visitors by the Otago Branch. On the next afternoon, the Annual Meeting of the N.Z.I.C. was held, and in the evening the Presidential Addresses of both Institutes were delivered by Professor F. P. Worley and Mr. G. A. Lawrence in an open meeting at which some sixty persons attended. The Institute of Chemistry of Great Britain and Ireland held its annual meeting on the 30th and in the evening the N.Z.I.C. held a further meeting at which the Code of Ethics was finalised and a discussion on fees took place. The Otago Branch was asked to set up a committee to consider the question of fees and to report to Council.

Delegates paid visits to the Physiological Dept. of the Medical School, Messrs. Gregg's spice and condiment factory, Hudson's confectionery and biscuit factory, and to Speight's Brewery.

Papers read and discussed during the Conference were as follows: Mr. W. Donovan initiated a discussion on standard specifications; Dr. R. Gardner read a paper on bacteriology in the Chemical laboratory; Mr. T. H. McCombs, M.P., exhibited some colour photographs and later opened a discussion on the co-ordination of research; Mr. L. H. James, speaking on photography as a supplement to chemical investigations, discussed cases of spurious coins; Mr. H. H. Edwards dealt with specifications for casein glue and tallow.

The Otago committee had arranged a three-day trip in the Southern Lakes district, including the Eglinton Valley and part of the road to Milford Sound, which was enjoyed by many visiting delegates.

ANNUAL CONFERENCE, 1937.

The Annual Joint Conference was held this year in Auckland concurrently with the Biennial Conference of the Australian and New Zealand Association for the Advancement of Science. A welcome to the visitors was tendered by members of the Auckland Branch at a morning tea held in Messrs. John Court Ltd. tea-rooms on January 12. Dr. J. C. Andrews, Chairman of the Branch, presided over an attendance of thirty-five.

The Annual General Meetings of the N.Z.I.C. and of the Institute of Chemistry of Great Britain and Ireland took place at Auckland University College on January 14. Professor Worley's Presidential Address is in part reported elsewhere in this issue of the *Journal;* the Chairman's address delivered to the N.Z. section of the parent Institute by Mr. F. H. V. Fielder, has been reported under the title

"Science and Nationalism" in the Journal and Proceedings of that Institute. Due to the fact that all members were attending the major Conference, no attempt was made to deliver papers at our own meetings.

Of the business discussed, special attention was paid to the proposed revision of our rules and to the form and future of the *Journal* of the Institute. A motion recommending to Council that the rules be revised during the current year was carried. A lively discussion on the *Journal* was introduced by Dr. Andrews. The necessity of having a publication was fully recognised, and appreciation was expressed of the high standard of the first issue, but there was a feeling that the *Journal* was in some respects too ambitious. Dr. Andrews then submitted a motion to the effect that it should take the form of a bulletin to be circulated at least quarterly, containing proceedings, correspondence, items of interest, information and accounts of papers delivered at Branch meetings; and that reprints of suitable papers by members of the Institute published in local or overseas journals should be secured and distributed. In supporting this motion, Dr. Briggs stated that, although the first copy of the *Journal* reflected great credit on all concerned, long intervals between successive issues would detract from its value. He was mostly opposed, however, to the publication of original papers therein and considered that New Zealand was already well provided for in this respect by the "N.Z. Journal of Science and Technology," and by the "Transactions of the Royal Society." Messrs. Dunn and Monro, members of the Publications Committee, strongly opposed the motion and drew attention to the vast amount of detailed and voluntary work involved and to the poor support received from Branches in supplying matter for publication. They expressed their conviction that at least some original papers were essential to the maintenance of a sufficiently high standard to attract the attention of abstracting bureaux overseas—as had already occurred in the case of the first issue. To this end, and also in the general interests of the profession, they appealed for more support from individual members of the Institute. Mr. L. S. Spackman considered that the apparent lack of support was due to a shortage of material and not to antagonism or indifference. He mentioned the difficulty experienced both in persuading speakers at local meetings to provide a written account of their lectures and also in taking adequate notes to be reconstructed for publication.

After several amendments had been proposed, Professor Denham finally moved that Council should consider the more frequent issue of the *Journal* and that its form be altered to suit country members. Stressing the fact that there had been nothing but praise for the

Journal but merely criticism of the general policy of the Institute with regard to its form, Dr. Andrews stated that the objective of bringing the matter before Council had been achieved. He, therefore, withdrew his motion in favour of that of Professor Denham, which was then carried.

Several other minor matters were dealt with and delegates were entertained at supper by the President and Mrs. Worley.

The final function of the Conference was the annual dinner at the Hotel Auckland on January 18. A total of forty-five were at the table, including a number of visiting Australian Chemists who were the guests of the combined Institutes.

(Due to unforseen circumstances, it has been necessary to report both the 1936 *and* 1937 *Conferences in this issue. The* 1938 *Conference in January next will be fully reported in the February issue of this Journal.)*

"CHEMISTRY AND CIVILISATION."

G. A. LAWRENCE.

(Chairman's Address to the N.Z. Section, Institute of Chemistry of Great Britain and Ireland—Dunedin Conference, 1936.)

Chemistry, like other sciences, is the result of the gradual evolution of observation and thought of mankind. As a science it cannot be traced back to any definite beginning, but certain periods have from time to time marked special progress, a gradual unmasking of the false and a steady march towards truth. Many centuries ago anything of the nature of inquiry into the unknown mysteries of the universe was looked upon as the exclusive right of the priesthood, and just as the witch doctor of the primitive races sought to mystify the people with their infusions and chants, so the priesthood of a later date sought to mystify their followers with their scanty and often inaccurate knowledge of scientific principles. Very few written records have come down to us to enable us to accurately gauge the extent of the knowledge of the Ancients on scientific matters, and we are therefore forced, very largely, to rely on the examination and analysis of the less perishable objects which have survived from those far-off days.

It is probable that the early Chinese were further advanced in their knowledge of matter and natural phenomena than dwellers of other parts of the world. The earlier peoples which inhabited India may have been possessed of knowledge of the sciences of which little or no records remain.

Egypt and the near east provide us with the best records of ancient knowledge. This is partly due to the activity of archaeological research in these regions and partly to written languages and to the climatic conditions which have helped to preserve for us records of the past.

The ancient Egyptians were well advanced in what may be dscribed as chemical technology, but owing to the absence of any fundamental theories, chemistry was practised more as an art than as a science.

It is not my intention to try and trace the evolution of the theory of chemistry but rather to give an outline of how chemistry has benefited mankind and to show how it has become a dominating factor in the progress of civilisation.

As stated previously the practice of chemistry during the pre-Christian era and probably in the early part of the present era, was looked upon as the prerogative of the priesthood and possibly to some extent of the more educated classes. Any chemical processes of the time were no doubt closely guarded. Chemical laboratories were attached to some of the Egyptian temples and it was probably in these that the elaborate methods of mummification were evolved, as well as the dyes, pigments, artificial gems, glass, enamels and other ornamentations used for sacred buildings. According to authorities on the subject it seems doubtful whether Egypt was the cradle of the chemical arts, but the art was often referred to as the "Egyptian Art," and the word chemistry has its origin in chemi, meaning the black land, which was another name for Egypt.

The process of tanning leather was probably one of the earliest of the chemical arts, and it is only in recent years that the ancient processes have been subjected to chemical control. White leather shoes, dating from prehistoric times, have been found in Egypt and during the time of the Old Kingdom tanned leather dyed all colours was used for furniture and documents were written on leather rolls. The processes used are not known but from the fact that common agents used for tanning such as lime, alum and several species of acacia were obtainable in abundance in Egypt, it is possible that they were used. The brewing of beer was a very early Egyptian art, and a number of varieties were known, such as bitter, flat, dark, sweet, foaming, etc. A number of yeasts were known: wine yeast, beer yeast, bottom yeast, yeast juice, etc., are referred to in the ancient writings. The process of making beer had much in common with present-day methods. The grain was sprouted, then ground up in mortars, moistened with water, and made into cakes and partly baked. The cakes were then broken up in water and fermented. Vinegar was used in the Ptolemaic period.

Bread has been made in Egypt from predynastic times. A number of varieties were known and "white" bread is mentioned in the ancient writings, but this probably meant bread made from flour derived from the lighter coloured grains. A passage in the Book of the Dead says:—"Let my bread be made of white grain and my beer from red grain."

The Egyptians were well acquainted with the use of cosmetics, and in the Book of Perfumes (Tunis) appears the following:—"They remove the inside of a lemon, fill it up with plumbago and burnt copper, and place on the fire until it becomes carbonised; then they pound it in a mortar with coral, sandal wood, pearls, ambergris, the wing of a bat and part of the body of a chameleon; the whole having previously been burnt to a cinder and moistened with rose water while hot." This preparation was used for painting under their eyes, etc. Perhaps owing to the eye strain caused by the heat and glare of the sun, eye paints were common in Egypt. Such statements as "to lay on the lids and lashes," "good for the sight," "to stop bleeding," have been found on eye paint containers. Staining the feet, hands and nails with henna, a dye obtained from Lawsonia inermis, was practised. Personal cleanliness was looked upon as a very important matter by the Egyptians, and although soap is not specifically mentioned in the records, certain directions are given in the early records for the boiling of oils and fats with alkaline substances and there appears to be every reason to believe that the use of soap as a detergent was known. Gold was used prior to 3400 B.C. for the purpose of gilding the teeth, finger and toe nails, and for plating objects made of the base metals. Gold was regarded as an expeller of demons and as an elixir of life. The gilding of metal was carried out by soldering gold leaf on to the base metal, but the work was so exquisitely carried out that no trace of the solder is visible at the contact point of the two metals. A copper pipe has been found 4.7 cm. in diameter with walls 1.4 mm. thick. This is part of a length of 400 meters, which was a drain in the Temple of King Sahura about 2500 B.C. The Egyptians were well versed in the art of metallurgy and the hardness of cutting edges which they obtained in their copper and bronze implements has been attributed to the effect of cold hammering.

Blown glass was unknown in early Egypt, but artificial glass beads were made prior to 3500 B.C., and glass was being manufactured on a large scale by 1375 B.C.

Meat was preserved by drying it, but fish and birds were preserved by the use of salt and the preservation of dead bodies was carried out by means of salt, before the art of mummification was introduced.

Pliny says that weaving was invented in Egypt—in any case linen was known in pre-dynastic times. The quality of Egyptian linen was such that it was almost transparent and of a silk-like texture. Some of the linens found belonging to the fifth dynasty contained 152 x 71 threads to the inch. Woollen garments were looked upon as unclean by the Egyptians, and silk was not known by them until the 4th century A.D. A number of dyes were known and used and fabrics of blue, red and yellow as well as many intermediate shades have been found. The dyes indigo and safflower have been identified and it is probable that the former was imported from India.

In the realm of medicine, the Egyptians were well versed in the use of drugs of vegetable and mineral origin. Their curative treatment was well intermixed with priestly incantations and mysticism, but many of their methods were based on sound principles. Stress was laid on cleanliness both inward and outward, and many of the diseases were considered to arise from over-eating and treatment freely embraced the use of emetics, purgatives, diuretics, etc. Pomades and ointments were used as a protection against the heat of the sun. In the Kahun Papyrus raw liver was prescribed for certain ailments.

The foregoing brief summary of the practice of chemical technology in ancient Egypt may be taken as fairly typical of the progress made in similar times in other countries such as Babylonia, Assyria and various countries of Asia Minor. It is fairly evident that before the beginning of the Christian Era there was a considerable interchange of ideas between the then civilised countries, and the growing knowledge of the use of natural products for every-day needs, for food and medicinal purposes, for building, ornamental and artistic purposes, must have had a considerable influence for the good of the peoples of the time.

As to the theory of chemistry, little or nothing appears to have been done until that rich period in Greek philosophy commencing about 600 B.C. Heraclitus (540-475 B.C.) stressed the orderliness of natural phenomena and his most important teaching was that all changes occur "by measure." This and the enunciation of the atomic theory by Democritus (460-370 B.C.) may probably be looked upon as the foundation or first inkling of the modern atomic theory. Anaxagoras (500-428 B.C.) held that there were a great variety of "seeds" which by various combinations produced all sorts of different objects.

Of Aristotle (384-322 B.C.) Thorp says he was "the greatest scientific thinker among the Greeks and exercised an authority almost supreme in Europe during the next twenty centuries." Aristotle, in common with the Greek philosophers of the time, made no effort to prove his theories by practical experimentation, but it is evident that he realised the danger of theory alone when he stressed the necessity of "trusting our senses more than our reasonings and our reasonings only when the results are in agreement with fact."

Early Christianity was hostile to philosophy and science, and it is not surprising that the subjects suffered a setback with the early advancement of Christianity. The closing of the Athenian schools of philosophy by Emperor Justinian had a serious effect on the progress of knowledge at the time. It is fortunate that the necessity of continuing the ancient arts, involving as they did the practice of chemical technology, at least kept the practical side of the science advancing.

The first 1500 years of the Christian era was a period of great difficulty in so far as the theory of chemistry was concerned, and had it not been for some of the Oriental nations the advancement of theory might easily have been retarded. The discovery in India of our present system of numerals and its introduction into Europe by the Arabs, and the translation of the old Greek works on science by the Arabs went a long way to preserve for posterity the knowledge already gained. The Arab Jabir, often referred to as the father of scientific chemistry, carried out a considerable amount of experimental work, and he was perhaps the first to insist on observation of experimental chemistry as a true basis of theory rather than pure speculation. At a later date, in England, Roger Bacon stressed the importance of scientific research and experimental verification of facts rather than reliance on books. In Europe the period was one of considerable darkness and chaos, old superstitions and beliefs were difficult to displace. The Alchemists searching for their philosophers' stone, the Great Elixir, the Great Magisterium, the Great Carbunculus and the theory of phlogiston all helped to cloud the issue, but they served a useful purpose in that they stimulated interest. A doctrine, even though it be a false one, is better than no doctrine at all because it stimulates and helps to keep alive the search for truth.

The idea of the possibility of transmutation is not to be wondered at. The love of wealth urged on experimentation and when at the present day we have people ready to believe in the economic possibility of transmutation we cannot blame the people of the middle ages for their persistent belief in the possibility. The Ancient Egyptians regarded gold as a sort of Elixir when taken in certain forms, and transmutation of metals was looked upon as possible although they were familiar with the fact that copper alloyed with certain other metals produced imitation or false gold. The Leyden Papyrus gives a number of details of treating copper for this purpose.

When we know from present day experience how the popular imagination is stirred by the spectacular and how discovery of real merit is passed over without notice, we may be certain that records of chemistry which have been preserved from early and middle ages dealt more fully with transmutation and the like while solid progress, which was undoubtedly being made, received scant attention.

During the period mankind had undoubtedly benefited to a considerable extent by the progress made in the art of chemical technology. The development in the use of iron and steel and the increased use of metals generally; improved and cheaper methods of manufacturing paper; the introduction of printing; improvements in the art of weaving and the increase in the number and variety of textiles; larger ships and better communications made possible the wide dissemination of knowledge, more clothing and more food for the masses. With the work of Robert Boyle and the formation of the Invisible College which finally grew into the Royal Society, we have the birth of chemistry as a science and the real beginning of the distinction between science and philosophy.

Up to this time the bulk of the people had lived close to nature. Foods and the general necessities of life were largely the products of their immediate surroundings. It was only the rich who were able to afford imported foods such as sugar, tea and wines. With the rise of industrialism in England great changes were brought about in the mode of living of the people. The gradual concentration of the workers in town areas made them more and more dependent on foods brought from a distance and there was less variety, less direct farm products such as butter, cheese and milk, and more white flour. While the employment of women in the industries, in many cases under deplorable conditions, introduced artificiality in the mode of living, and infants were not breast-fed to the same extent as formerly, with the consequence that deficiency diseases became more prevalent. Moreover, the rapid advance of industrialism outstripped the progress of science and our knowledge and methods of coping with new problems was practically non-existent. Just what effect this had on the health of the nations no one can estimate, but the cause and cure of deficiency diseases and malnutrition are, one might say, only just being elucidated. The discovery of vitamins and the chemical identity of the glandular secretions, to mention only two lines of chemical research, have played, and will in the future play, a great part in the elucidation of therapeutic problems. In the growing artificiality of the rearing of infants, and in those countries and sections of communities where variety in diet is limited, the discovery and study of vitamins and the vitamin content of foods is of the utmost importance, but it is feared that there has been unnecessary exploitation of the public in such countries as New Zealand where a diet within reach of the average person or family is well supplied with these bodies. With the knowledge we now have at our disposal it is the sacred duty of those members of our profession who have charge of the manufacture of foods to see that no process is applied which will tend to destroy or alter the natural chemical constituents. It is an unfortunate fact that there is still a number of people who manufacture and prepare foods for the public consumption who have no fundamental knowledge of the chemical changes which might take place, but there is some consolation in the fact that all leading countries of the world now have food laws to protect the public.

In the foregoing I have endeavoured to outline the progress of chemistry as an art and its steady advance with the civilisation of the people. From the time of Boyle to about the middle of last century the industries were not influenced to any considerable extent by chemistry as a science. If, however, we examine the work carried out during the period, we find that it was rich in discoveries whose real value to industry and civilisation has only recently become apparent. In the discovery of the gases carbon dioxide and ammonia by Priestley in 1773, and the liquefaction of these same gases by Faraday in 1829, was the germ of that vast industry modern refrigeration. The benefit of this industry to civilisation is incalculable. Then again it was Faraday who first isolated benzene from bone oil, while Hofmann, in 1845, found benzene was a constituent of coal tar. Neither of these scientists knew that this substance would one day provide the basis of the great coal tar dye industry, and it fell to the lot of Perkin in 1856 to discover the first coal tar or aniline dye. This discovery not only marked the commencement of the great synthetic dyes industry but it opened up vast and hitherto unknown fields of research in organic chemistry which led to the discovery of new explosives, disinfectants, medicines and many other products which are now everyday commodities.

The manufacture of synthetic dyes was one of the great tragedies of British chemical industry. Great Britain, with her huge coal reserves, was in a unique position to build up a great industry in this direction, and it must be admitted that Perkin, Nicholson, Caro and Granville Williams built up great businesses and retired with handsome fortunes derived from the manufacture of dyes, yet the industry was allowed to languish and fall into the hands of the Germans. It is fortunate that post-war efforts in Great Britain have largely restored this lost business.

Along with the gradual mechanisation in industry and the increase of scientific management of industry during the past 20 years there has been a growing fear that the benefits derived are being outweighed by new problems arising from these new conditions. On the one hand we have tremendously increased production in every need which should go to make the lot of the average individual happier, and on the other hand we have the ever increasing army of unemployed which is steadily but surely breeding a hopelessness of outlook for the future. We have people seriously advocating the temporary cessation of scientific research in order that world affairs might have time to reach a stage of equilibrium. Such action is, of course, impossible; the many thousands of workers the world over are not going to cease work at the strike of the clock. A solution to the present difficulties is more likely to be found with a continuance of the efforts than adopting the Macawber-like attitude of waiting for something to turn up. On the question, Dean Inge says: "I cannot believe that technical invention will in the long run prove to be a curse to mankind so that like the Erewhonians of Samuel Butler we shall have to smash all our machines."

There seems little doubt that certain countries, including Great Britain, have tended to swing too far along the road of industrialism to the detriment of agricultural pursuits. The prospect of a country becoming almost entirely an industrial centre is not a happy one, nor does it seem desirable for some countries to remain entirely agricultural. Apart from the obvious military weakness under such conditions it is unpleasant to think of industrial workers being entirely removed from the amenities of rural surroundings, and it is equally detrimental for rural people to be entirely removed from the cultural influence afforded by larger cities and towns. The lessons which were learned from the last war have shown the undesirability of predominant dependence of one country on another for necessities, and the struggle since that time for national sufficiency has at least had the effect of stimulating some of the industries which had been flagrantly neglected. The failure to recognise the value of scientific research in Great Britain prior to 1914 was no doubt due to the fact that she was the first of the modern industrial states. The demand by the rest of the world for her products had brought about such colossal prosperity that the nation sat back as it were with the idea that the state of things would continue indefinitely, with the result that a state of *laisser-faire* set in. Germany, on the other hand, which it is said did not possess a single large factory prior to 1850, anxious to establish external markets, paid assiduous attention to research in industry, with the result that by 1914 she had built up a huge export trade and had far surpassed Great Britain in the application of chemistry to industry. Dean Inge says: "Germany was the first scientific state, and it was nearly too strong for the rest of the world banded to destroy it." Had Germany not gone to war in 1914, but continued with peaceful commercial penetration, it is hard to imagine what the state of its world trade would have been to-day. One thing is certain; we cannot afford to disregard the possibilities of scientific development. The production of petrol and other oils from heavy oils and from coal is very largely due to the result of the research work of the Germans and the great works just recently erected in England by Imperial Chemical Industries subsidised by the British Government for the production of petrol from coal is largely based on German patents. Some people have pooh-poohed the possibilities of the economic production of synthetic wool which has recently been reported from Germany. We cannot afford to ignore these possibilities. The dimensions of the present day production of artificial silk is an object lesson as to what may be achieved in the realms of synthetic chemistry. Many of us in our student days listened with awe when our favourite professor described in detail the methods by which he produced "enough sugar to sweeten a cup of tea from one of his old cotton shirts." To-day we know that synthesis by breaking down complex molecules to more simple molecules is comparatively easy. Not many years ago compounds which we encountered in our studies of organic chemistry and looked upon as curiosities only to be seen on rare occasions and then only in small quantities are now being produced in hundreds and thousands of tons. The development of the lacquer and solvent industries affords a wonderful example of the possibilities of chemical synthesis. Why, therefore, should the possibility of building up a complex molecule, such as that present in wool, be ignored. It is a good thing to be cautious in accepting new ideas, but an attitude of contempt, indifference or bias cannot be defended. Speaking on bias, the late Mr. Justice McCardie once said: "No more potent cure for bias is to be found than the study of science, of history, of economics and of law. Enthusiasm is the enemy of truth unless it be guided and restrained by the love of truth."

"I should myself ever wish to deal with the subject of truth in the spirit of a fearless and unbiassed man of science. How profoundly different would our public life be to-day if that spirit had been adopted by those who profess to deal with the grave social and economic problems that beset the nation. Public controversy in this country will never, I feel, rest on a righteous basis until the spirit of the fearless and unbiassed scientist is recognised by all who address the people."

One great benefit the British derived from the Great War was the fact that it brought the nation face to face with the fact that they had slipped badly in their neglect of science. The production of heavy chemicals was an industry of considerable dimensions prior to 1914 and the annual output of sulphuric acid was looked upon as a reliable index as to the state of national prosperity, but when the war started the production of oleum and the potential facilities for its production was far below those required for the manufacture of explosive for prosecuting the war. Just what effect this had on the early progress of the war no one can estimate, but we do know that our men were for a long time carrying on without adequate supplies of the ordinary necessities of war while our opponents were fully supplied. It is fortunate that the country had many chemists of outstanding ability, many were recalled from the front lines and the problems of increasing production of explosives and other necessary chemicals tackled. When it is realised that in many cases whole plants had to be erected and the processes started from bedrock considerable credit is due to the men responsible. The post-war years have been a period of renaissance in British Chemistry and one may say that the nation is only just beginning to recapture some of the dye trade which started with Perkin's discovery of aniline violet.

The fact that the last war was a war of science has unfortunately given the public an impression that chemists are all the while searching for new and devilish explosives, chemicals, gases and devices for use in war. The fact of the matter is that very few chemists are engaged in the production of explosives and general munition work, while hundreds of thousands are engaged in supervising research and production of almost every article required for the good of mankind. In a recent address, Professor E. F. Armstrong, speaking on this question, says: "In peace times chemicals are definitely and absolutely not munitions, though there are cranks sufficiently crazy to claim the contrary. Neither chemists nor chemistry make war. In war everything becomes a prospective munition, from a lump of coal and a blade of grass to the most complex optical instrument. Glycerin and nitre have very different uses in peace and war."

Various prophecies have been made from time to time to the effect that the exhaustion of some of the necessities of mankind would occur. Many years ago it was stated that the soils of the world would become barren because of a shortage of nitrogenous manures. Since that time the world has witnessed the establishment of one of the greatest chemical industries—that of the fixation of atmospheric nitrogen and the production of synthetic nitrogenous fertilisers as well as many other compounds for other purposes. The establishment of this industry guarantees for all time an adequate supply of nitrogen. More recently it has been stated that our mineral fertilisers are likely to become depleted because they are leached from the soil and finally find their way to the sea. One might well inquire what becomes of these minerals when they enter the sea and whether there is any valid reason why they should not be recovered from the sea when depletion of land deposits makes this necessary. Our knowledge of the deposits at the bottom of the sea is at present fairly limited but there is every possibility that at certain depths there may be some rich deposits of phosphates, the recovery of which may not offer insuperable difficulties. One is treading on dangerous ground in making any prophecies for the future. Scientific discovery during the past 20 years has been so rapid as to cause a certain bewilderment but it is fairly safe to prophesy that the population of the world will be provided with plenty of the necessities of life for a long time to come. There may occur shortage of certain materials which we now look upon as necessary but there is always the possibility of other materials replacing them. The present day extent to which aluminium is replacing other metals is an example of this trend. With regard to the production of foods, the use of fertilisers, irrigation and our knowledge of agriculture generally has enabled man at the present day to grow crops on land which would have otherwise been barren, but as to intensive cultivation and the full utilisation of land it is doubtful if we are to believe Prescott, whether we have advanced much beyond the Peruvians. It has been suggested from time to time, obviously by people who are carried away by the wonders of modern science but with little or no personal knowledge of the subject, that the time will come when food will be so concentrated that one or two tablets will suffice for a meal. For this to be possible there would have to be some fundamental changes in the human machine, or the discovery of foods of far higher calorific values than we have to-day. In terms of energy we require 3,000 or more calories per day. To supply this energy we require ¾ lb. of fat or oil or 1½ lbs. of sugar. These quantities would make rather cumbersome tablets and the diet would be very unbalanced.

Mankind must leave the production side for the time being and concentrate on the problem of distribution. In our own country alone production has in the last few years increased enormously, yet there have been anything up to 80,000 people unemployed. The same state of affairs exists in nearly every country of the world. The people blame the Governments in power at the time for these conditions, and at election time the opposing parties make political capital out of it, yet we know that the cause is much more fundamental. Governments may adopt palliative measures but the real solution of the trouble lies much deeper. It would seem that there is a bad flaw in the economic system of the world and perhaps a certain writer is correct when he says: " Economics is in a state of alchemy."

The growing trend of curtailing the number of working hours and so employing more work people is a fruitful line of research. The plea for a wider adoption of this scheme as a cure for unemployment is being extensively used as a political catch cry but the fact is often lost sight of that its adoption introduces another problem, that is the proper utilisation of leisure time. The shortening of hours means increased leisure for the masses but it does, or should not, mean increased idleness and one of the problems our educationalists will have to face as their contribution to the problem is the education of the people to make the best use of leisure. It will take time to bring these conditions about, mechanisation of industry with the gradual abolishing of unhealthy conditions of employment, shorter hours and profitable utilisation of leisure hours should in the long run prove a boon to mankind rather than a curse.

At a recent meeting a speaker criticised an authority because he suggested that malnutrition in this country is largely due to the average housewife's lack of knowledge in buying suitable foods to give a balanced diet, rather than lack of adequate purchasing power. A certain minimum amount of money is undoubtedly necessary to cater for a family but lack of a basic knowledge of dietetics means all the difference between correct nutrition and malnutrition, especially when purchasing power is limited. Under modern conditions of life a knowledge of dietetics is absolutely essential, and we as chemists should do everything in our power to encourage this side of education.

We cannot measure the benefits chemistry has brought to mankind in terms of happiness because happiness is merely a relative state. It is possible that the relative measure of happiness of the people of the middle ages with their simple rural existence was just as great, if not greater than the happiness of a similar class to-day. Chemistry has brought a considerble material benefit to mankind. The very foundation of modern civilisation is based on chemistry, and it is difficult to find any department of human activity which is not dependent on it. The tendency towards equality amongst the masses is largely due to its influence and we may look forward to a greater influence in the future. Scientific methods of packing, storage and transport has brought tropical as well as temperate food products within the reach of the masses of all parts of the world. Chemistry has unearthed a vast variety of medicinal preparations and is ever placing in the hands of the medical man new remedies for the prevention and cure of diseases as well as anaesthetics for the relief of pain and the conduct of painless operations. Chemistry has improved the old textiles and introduced many new ones, while the range of colours for every possible use is a matter of wonderment. Dress fabrics and other articles of wearing apparel are now within the reach of the masses which would have been the envy of the rich a few decades ago. On every hand can be seen the results of applied chemistry, in the finishes of the modern homes, in the specialised steels and other metals used for aeroplanes, motor cars and in modern machinery and construction. The application of science has improved the lot of man in the industries and removed the drudgery in many occupations. There is still a long road to travel before many of these problems are put on a satisfactory basis. No one can see the end of the road or the ultimate goal, and as Stevenson said: "Little do ye know your own blessedness, for to travel hopefully is a better thing than to arrive, and the true success is to labour."

In the past the scientist has been too taken up with the immediate problem to pay adequate attention to administrative matters, but the time has come when the problems of the world should be approached and studied from the scientific viewpoint. The slogan for the world to-day should be: "More science in administration." The problems arising from our present state of civilisation cannot be successfully coped with by the old hit or miss practical methods nor is it safe to institute correctives based on purely theoretical considerations. The questions must be approached with due appreciation of the practical and the theoretical. Just as in chemistry the main reaction is nearly always accompanied by a subsidiary reaction, so in administration the corrective for one problem very often gives rise to another problem, and it is the full realisation and appreciation of these facts that is so necessary. The exacting theoretical training of the chemist, mellowed and disciplined by his experience in practical chemistry, produces a critical and detached judgment probably superior to any other scientific calling which should eminently qualify him to tackle the problems of the day.

THE BRANCHES.

AUCKLAND.

Papers read—

- "Chromium Compounds and their relation to the Werner Co-ordination Theory in the Manufacture of Leather."—*P. White.*
- "The Analysis of Wood."—*Professor F. P. Worley.*
- "Tests for the Porosity of Tin Plate."—*R. T. D'Anvers.*
- "The Manufacture of Coal Gas."—*R. Stansfield.*
- "The Bacteriology of Milk."—*W. C. Neil.*
- "Odds and Ends Evening."
- "The Manufacture of Cement."—*E. Leese.*
- "Biological Tests of Blood."—*Dr. W. Gilmour.*

CHROMIUM COMPOUNDS AND THEIR RELATION TO THE WERNER THEORY IN THE MANUFACTURE OF LEATHER—*P. White.*

In the manufacture of leather we are able to teach the ancients nothing; as in its class Morocco leather is still the best, although the process is 3000 years old; in fact the only new materials used are the chromium compounds which were introduced in 1878. This new process involved at first the use of a basic chromic chloride, but this was replaced by chrome alum during the war.

Two essentials for a tanning liquor are, firstly, a high molecular weight, and secondly, free OH groups. In practice a difficulty was experienced in reproducing exact conditions which led to very rule-of-thumb methods being employed. For example: (1) If the chrome alum is dissolved hot it has a different pH from that dissolved cold, (2) After standing, although the basicity remains constant, the pH alters, (3) The alkali used to render the chrome alum basic has a marked effect, (4) If bichromate was used, a different tan liquor was obtained if the acid was added before the reducer or *vice versa.*

Even to the chemists of the day these effects were baffling, and consequently little headway was made in the scientific control of tanneries. However, in 1893 Werner enunciated his co-ordination theory. According to this theory the familiar $CrCl_3.6H_2O$, could, according to the physical conditions of solution, assume the forms $[Cr(OH_2)_6]\,Cl_3$, $[Cr(OH_2)_5\,Cl]Cl_2 + H_2O$ or $[Cr(OH_2)_4\,Cl_2]Cl + 2H_2O$, and as the effective concentration of OH is seen to be different in each of these, the tanning power of $CrCl_3.6H_2O$ will be different according to the method of solution.

It was stated that a tan liquor has of necessity a high molecular weight. In the case of chromium compounds, Werner's theory indicates how a system of polymerisation termed *olation,* may take place through the OH groups involving secondary valencies. This olation explains how the pH of a chromium solution may alter on standing, although the acidity as titrated is unaltered.

From these examples it is seen how Werner's theory explains the facts as observed in the tanning industry.

THE MANUFACTURE OF COAL GAS—*R. H. J. Stansfield.* In outlining the properties of various types of coal in relation to their gas-producing properties, the speaker outlined the reasons why Gas Companies prefer Australian coal to the local, the chief advantages of the former being that it is richer in gas, the coke does not swell, it is much more constant in analysis, and the sulphur content is lower. These advantages offset any slight differences in price.

The speaker outlined the evolution of the present type of continuous vertical retort from the horizontal, the inclined and the intermittent vertical types. The modern continuous process possesses the advantage that the gas is not " cracked " to the same extent as in the intermittent type. About 15% of the coke produced is employed in forming " producer " gas to heat the retorts, after being preheated by waste flue gases.

The refining stages were detailed and well illustrated by lantern slides. Referring to the purifiers, the speaker stated that 35 reactions are known to take place, with production of such substances as $(NH_4)_2S$, NH_4CNS, urea and prussian blue. Although the limonite, obtained from near Whangarei, removes H_2S, carbon disulphide is unaffected; but may be reduced by passage over nickel at 400° to $H_2S + CH_4$, followed by reabsorption over limonite. Benzol to the extent of 11 gallons per ton may be recovered and is used to drive the Company's motor vehicles.

The lecturer concluded by stating that many of the possible by-products were not recovered locally, due to the comparatively small scale of operations and lack of demand in New Zealand for these products.

THE ANALYSIS OF WOOD—*F. P. Worley.* The analysis involves the determination of ash, moisture, cellulose ($\alpha\, \beta$, and γ), lignin, both hot and cold water extract, the alcohol-benzene soluble content, methoxy content, alkali soluble, and total pentosans. Even in a routine laboratory a complete analysis involves at least a week's work after the sample is prepared.

Preparation of Sample: The sample is obtained from the sawdust from a circular saw, passed through an 80 mesh sieve and retained on a 100 mesh. If necessary the sawdust may be ground. The sample is allowed to assume an air-dry condition. *Moisture*: This varies considerably from about 5% in North American wood to 8-12% in English. The determination is best made by distillation with xylol; and all results are calculated back to the dry weight. *Alcohol-benzene solubility* is carried out with the constant boiling mixture (approx. 1:2). This extracts the resins, tannins, alkaloids, etc. *Cellulose*: This is determined by successive chlorinating of the residue from the above and extracting with 2% sodium sulphite, under standard and specified conditions. The cellulose is precipitated by boiling, filtered off and weighed. Anything up to 12 chlorinations may be necessary for complete extraction of the cellulose. *The Lignin* is determined as a residue from the alcohol-benzene extraction after treating with 72% sulphuric acid when the celluloses are hydrolysed and the residual lignin filtered off and weighed. *The Pentosans.* These are related to cellulose but built up of pentoses instead of hexoses. The pentosans are estimated after hydrolysis by dehydration to furfuraldehyde which is distilled off and weighed as its complex with phloroglucinol.

The empirical nature of these determinations was greatly emphasised, it being stated that values were not comparable unless carried out under identically similar conditions using similar apparatus with careful attention to the time of each operation, the amount of washing, temperature of drying, etc.

WELLINGTON.

Papers read—

"B.P. Galenical Preparations."—*F. Morgan.*
"Blood Transfusion in Modern Medicine."—*Dr. P. P. Lynch.*
"Gas—The Weapon of the Future."—*L. H. Davis.*
"Crystallisation of Iron Oxide at High Temperatures."—*J. J. S. Cornes.*
"Micro Determination of Cobalt."—*K. J. McNaught.*
"Spray Residues on Cabbages."—*P. J. C. Clark.*
"The Chemistry of Cheddar Cheesemaking."—*Dr. R. M. Dolby.*

FILMS OF INDUSTRIES. At the first meeting of the year, films illustrating industries in which there was much to claim the attention of the chemist were exhibited in the Blue Triangle Hall. This meeting, which was open to the public and well attended, was addressed by Mr. T. H. McCombs, M.P. The following films were shown, a short lecture and explanatory comment being given with each: "The Manufacture of Bread" (Mr. R. L. Andrew), "Leather" (Mr. P. White), "Pottery" (Mr. L. R. L. Dunn) and "The Manufacture of Pig Iron" (Mr. J. J. S. Cornes).

GAS, THE WEAPON OF THE FUTURE—*L. H. Davis.* For military purposes "gas" can be defined as any type of chemical (solid, liquid or vapour) capable of inflicting injury on the human body.

Its military purpose is to produce dislocation of the organisation of an enemy, producing casualty and panic rather than death. Claims have been made that the after-effects of being "gassed" are, on the whole, transitory. Medical authorities have not yet produced a final statement on this point, however.

Gases are either persistent or non-peristent according to the period after liberation during which they are or may become effective. The former differ from the latter, which are true gases, in that their persistence is due to their being liquids which volatilise relatively slowly from their resting place.

A classification of gases according to their physiological action is as follows: (a) Pulmonary irritants, lethal in their action, of which examples are chlorine, phosgene, diphosgene and chloropicric acid, (b) Sternutators, or sneezing gases which are arsenical in nature, (c) Lachrymators, or tear gases which produce temporary helplessness, (d) Vesicants, or blistering gases of which mustard gas is probably the most notorious, (e) Paralysants, or poisons of the nervous system such as hydrogen cyanide, (f) A type, including carbon monoxide, which interferes with the functions of the blood.

The chemistry of tried and proposed gases is in general concerned with relatively simple compounds of the lighter elements of groups 5, 6 and 7 of the periodic table. Molecular complexity tends to reduce effectiveness. Thus it would appear that there are more or less definite limits to the invention of new types of poison gases.

In answering questions, the lecturer covered matter dealing with protective measures against the dangers of gas.

THE CRYSTALLISATION OF IRON OXIDE FROM SODA-BORAX FUSIONS AT HIGH TEMPERATURES—*J. J. S. Cornes.* In the ordinary crucible assay for gold and silver, it is the usual practice to add borax to the soda of the charge especially if the ore contains much metallic oxide. If the same procedure be adopted in the routine soda fusion for silicate (with, for example, an iron-sand) in a platinum crucible over a good blast, it is found that as the melt cools the whole mass appears suddenly to crystallise—with the extrusion of green manganate impurities—to a scaly form of iron oxide suggesting micaceous haematite. The fusion-mixture used was five parts anhydrous sodium carbonate to one of anhydrous borax and about five grams of the mixture was used to half a gram of ore—a much larger excess than in the fire assay for gold. No crystals were obtained in any but platinum crucibles. The crystals always contained varying small amounts of soda and larger percentages of water.

In "Study of Ore Deposits," by F. H. Hatch, the action of volatile "mineralizers" such as boron and fluorine in the neighbourhood of granite intrusions (the "aura granitica" of Elie de Beaumont) is emphasised. Many iron-ore deposits are found at the contact of bathyliths with limestone—e.g., on the Island of Elba, and "the occurrence of well crystallized haematite is a feature of these deposits." The author, therefore, wrote Sir William Bragg concerning the suggestion that micaceous iron oxide might have originated in nature in much the same way as in the platinum crucible. But although he referred the matter to the Geological Survey and Museum, London, the reply seemed still to leave much to be said on both sides. The matter is, therefore, being referred further to the Washington Geophysical Laboratory for comparison with their work on the iron-oxide systems.

MICRO-DETERMINATION OF COBALT—*K. J. McNaught.* For the analysis of mineral supplements used in the treatment of stock ailments a sensitive colorimetric method for the determination of cobalt was required. The better known methods, which were briefly outlined, were not sufficiently sensitive. Nitroso R-salt, a derivitive of α-nitroso-β-naphthol, was found to be quite the most satisfactory and an improved technique was developed whereby the method could be applied down to 0.2γ cobalt or even lower.

The reagent itself is liable to be destroyed by oxidising and reducing agents but, once formed, the cobalt complex is stable to boiling nitric acid. The resulting colour is a reddish orange with Lovibond yellow units always in excess of red. For the work undertaken Nessler tubes were preferred, especially as the amounts being estimated were often very small. Macro quantities of iron had to be removed and, as losses of cobalt by the hydroxides precipitation method are very great, a method had to be devised for the removal of the iron by ether, using a type of Soxhlet extraction apparatus.

Some analyses for cobalt in limonites, soils and animal organs were given and a brief reference made to the physiological significance of cobalt in animal nutrition, with special reference to bush-sickness.

SPRAY RESIDUES ON CABBAGES—*P. J. C. Clark.* Consequent upon the use of lead arsenate in the control of white butterfly, the problem of ascertaining the amount of spray residue has arisen. The New Zealand Regulations under the Sale of Food and Drugs Act, 1908, make no reference to arsenic or lead in vegetables other than in tins and hence the presence of either is not allowed on the fresh vegetable. The limit for arsenic on fruit such as apples and pears, however, is fixed under this Act at 1/100 grain of As_2O_3 per pound; the limit for lead is *nil.*

Suitable analytical methods for the determination of very small amounts of arsenic and lead in cabbages required development, and during the past two seasons large numbers have been sprayed and then examined for residues. The method found to be satisfactory for arsenic was as follows: The cabbage is subjected to wet oxidation by nitric and sulphuric acids, the arsenic is distilled off with hydrochloric acid and the distillate evaporated to dryness after the addition of nitric acid; the residue is dissolved in sulphuric acid and the arsenic determined either by the electrolytic Marsh method or (in the case of larger amounts) by titration with N/100 iodine after reduction to the arsenious form. The determination of lead presents greater difficulties, but a method based upon the use of dithizone on the residue from the arsenic distillation is showing promise.

Analyses indicate that, with a lapse of five weeks between spraying and harvesting, the amount of residue on the heart of the cabbage varied between 0.0001 and 0.0005 grain As_2O_3 per pound, compared with 0.02 to 0.20 grain As_2O_3 per pound on the whole cabbage.

There is a great need for a spray material to replace lead arsenate which will be toxic to insects but not to man. This need is being met in Derris dusts and sprays, where the toxic principle is rotenone.

THE CHEMISTRY OF CHEDDAR CHEESEMAKING—*R. M. Dolby.*

Cheesemaking is an ancient art. The general principle employed is the removal of the greater part of the moisture from milk after the latter has been coagulated by acid or rennet. This concentration improves the keeping quality which is further enhanced by the addition of salt. Cheese contains almost all the fat of the milk, the greater part of the protein and more than half of the minerals.

Little was known of the reactions involved until large scale manufacture began to replace that in farm dairies and attempts had to be made to reduce the art to a scientific basis. The earliest systematic investigation was that of Lloyd in England in the 1890's. Lloyd showed that the acidity of the whey increased throughout the process and that it was the combined effect of acid and heat which expelled the moisture from the curd. It was not till later that the work of bacteriologists showed that the increase of acidity was due to a fermentation of lactose to lactic acid by bacteria. Lloyd suggested the use of the "acidimeter" for timing operations by the acidity of the whey, and Van Slyke introduced the method into America. The latter worker made a fuller study of the fermentation of lactose in curd and the changes in the mineral compounds. It was also shown by him and by Continental workers that in the ripening of cheese there is a breakdown of the protein into peptones and simpler products.

Sammis at Wisconsin demonstrated that the rate of separation of moisture from the curd was determined by the size of the pieces of curd and by the temperature. He also showed that acid production took place almost entirely within the curd particles as almost all the bacteria are enmeshed in the curd.

Cheddar cheesemaking in New Zealand is carried out, under average conditions, as follows:—

The milk is pasteurised by heating to 155-160°F. for 30 seconds, cooled to 88°F., and then run into vats, and 1-1½% of "starter" added. The starter is a culture in milk of bacteria selected for their power to produce acid and withstand the temperatures employed in cheesemaking. After a ripening period of about 30 minutes, rennet is added in the proportions of 3-4 oz. per 100 lbs. milk and the resulting curd when sufficiently firm is cut into ½ inch cubes. The temperature is then raised to 98-100°F. for the "cooking" process to hasten expulsion of whey. Some 2-2½ hours after cutting, when the whey acidity corresponds to 0.15-0.18% lactic acid, the whey is run off from the vat. The curd particles, which by this stage have shrunk to the size of a pea, are piled at each side of the vat, leaving a channel for the whey to escape. The particles soon mat together to form a solid mass which is cut into slabs for the "cheddaring" process. Two to 2½ hours after "running," when the whey acidity is about 0.80%, the curd is cut into strips with a curd mill. About an hour later salt is applied in the proportion of 2½-3% of the weight of curd expected from the quantity of milk used. The salt is sprinkled on the curd and thoroughly stirred in. The flow of whey from the curd, which has almost ceased after milling, recommences when the salt is added. Half-an-hour after salting the curd is packed into hoops and pressed. The next day the cheese is removed from the hoops. It is cured for 14 days in the factory at about 60°F. and is then railed to the grading store; throughout the period till it is sold in England is kept at 45°F.

While the whey acidity is used as the chief guide in timing the various operations in cheesemaking, the acidities used must be varied to suit different types of milk and starters and the cheesemaker has to rely to a great extent on his own judgment. The feel of the curd is the only indication he has of the moisture content.

Chemistry of Cheesemaking. Milk contains, on the average, 4% of fat, 2.8% of casein, 0.75% of albumin, and 5% of lactose. The chief minerals are calcium and phosphorus occurring as calcium phosphate and calcium caseinate. The albumin is not coagulated by rennet and is almost all lost in the whey. The curd resulting from the coagulation of the casein contains nearly all the fat and most of the minerals. A certain amount of the casein is lost, apparently as a breakdown product formed by the rennet action. The casein loss is very variable. It averages about 4.5% of the casein in the milk but losses varying from + 12% to – 3% have been reported. Some 6% of the fat in the milk is lost in the whey. Most of this loss occurs at cutting, and incomplete coagulation or vigorous stirring of the curd at this stage increases the losses. The whey at running comprises some 90-95% of the total whey lost and most of the losses of solids occur in this whey. Although the later wheys have a high solids content the quantity is too small to contribute greatly to the actual weights of solids lost.

As the acidity increases, the insoluble calcium phosphate and calcium caseinate in the curd are converted to soluble acid calcium phosphates and calcium lactate which pass into the whey. The acidity developed, therefore, governs the mineral losses. Since some 90% of this loss takes place at running the acidity at this stage is important in controlling the amount of calcium and phosphorus left in the cheese. On the average some 60% of the calcium and 57% of the phosphorus are retained but with higher running acidites these quantities will be reduced.

The concentration of lactose and minerals in the whey is much lower just after salting than just before. This dilution was at first thought to be due to a liberation of bound water from the curd by the action of the salt but later it was concluded to be an osmotic effect. It was also found that a Donnan membrane equilibrium governed the partition of electrolytes between curd and whey. Evidence has been found for the existence of bound water in curd but attempts to make accurate measurements of the quantity have encountered many difficulties. The amount of bound water in a cheese is likely to have an influence on the body of the cheese and on the rate of drying out when cut.

Cheese Ripening. The lactose incorporated in a cheese is gradually fermented by the starter bacteria and after a week or ten days has usually completely disappeared. Only where abnormally large amounts are present or where the starter bacteria die out very quickly does any remain after this time. In normal circumstances the starter bacteria survive for two or three weeks and then disappear. Their place is soon taken by other bacteria, the lactobacilli, which although present at first in infinitesimal numbers find cheese an ideal medium in which to multiply. These organisms do not attack lactose to an appreciable extent. The pH of cheese falls as long as fermentation of lactose is continuing and then shows a gradual rise throughout the remainder of the ripening period.

The principal reaction in the ripening of cheese is the breakdown of the protein by the rennet retained in the curd. This breakdown changes the body of cheese from rubbery to mellow. The flavour developed in mature cheese, while at first thought to be due to protein breakdown products is now considered to be due to other products of bacterial origin.

CANTERBURY.

Papers read—

- "A Phase Rule Investigation of the System Phenol-Water-Mecuric Chloride."—*J. Packer.*
- "Demonstration of Tag-Hepenstall Electric Moisture Meter and the Glass Electrode."—*E. W. Hullett.*
- "The Nature of the Chemical Link between Atoms." (Chairman's Address).—*J. Packer.*
- "Colloids."—*Dr. R. O. Page.*
- "The Soils of the Nelson District."—*T. Rigg.*
- "Colloids Applied to Agricultural Science."—*Dr. M. C. Franklin.*
- "Recent Advances in the Chemistry of Cement and Concrete."—*J. Packer.*
- "Colloids in Bread Making, and Demonstration at the Wheat Research Institute."—*E. W. Hullett.*
- "The Vitamins."—*Dr. J. Melville.*
- "Some Progress and Problems in the Gas Industry."—*F. W. Belton.*

THE NATURE OF THE CHEMICAL LINK—*J. Packer.* The forces which can act between atoms made up of positive nuclei and electrons are of two kinds: electromagnetic and gravitational, but the latter are quite insignificant compared with the former. Valence forces, cohesion, co-ordination, etc., are different manifestations of these electromagnetic forces. These same forces lead to two different kinds of valence bonds between atoms, (i) electrovalency, where the atoms are held only by Coulomb forces, and, (ii) covalency (including co-ordination as a sub-species), where the atoms are actually *linked* to one another in the older sense of the term. There is a third way in which atoms and in fact all molecules attract one another, which is due neither to the transfer nor to the sharing of electrons and is therefore not a form of valence, but is the result of electronic interaction and deformation. This leads to forces between the atoms and molecules, called the van der Waals forces, which are weaker than those involved in valence bonds. In the different states and forms of matter these three forces are of widely different relative importance.

The properties of salts, metals, alloys and inter-metallic compounds, organic compounds, and the compounds formed between nonmetals, and substance consisting of giant molecules, can all be interpreted in terms of these three kinds of interaction between atoms and molecules.

Physical methods of investigation now make possible the measurement of such characteristics of the chemical link as, (i) length, (ii) strength, expressed either as energy needed to break the link or the restoring force called into play on stretching, (iii) polarity, and (iv) the angles between links. Such measurements have greatly extended our knowledge of the spatial configuration of inorganic molecules and given a physical basis to the stereo-chemistry of organic compounds.

COLLOIDS—*R. O. Page.* In this brief survey of such a wide field it seemed advisable to review only the more successful applications of the methods of classical physical chemistry to the study of colloidal behaviour. In any liquid there is a monomolecular surface film in which all the molecules have their active portions drawn inwards, their inactive portions forming the surface layer. Thus alcohols and the liquid hydrocarbons have the same surface energy, as the surface in each case consists of methyl groups. The stability of an emulsion is determined by a similar orientated film of an emulsifying agent, all of which have long molecules with a terminal polar group. In an emulsion of oil in soap solution, for instance, the methyl groups are in contact with the oil, while the positive ion is drawn towards the water, the nature and stability of the emulsion being determined by the shape of the molecule forming the surface film. Thus soaps of the alkalis form oil-in-water emulsions because the cross-section of the metal ion is greater than that of the fatty acids; but with soaps of the alkaline earths, the reverse is the case, so they form water-in-oil emulsions.

There is around a positively charged colloid produced either by the formation of an orientated surface layer of the above type or by ionisation, positive ions on the surface of the particle, balanced by an equivalent number of negative ions in a thin layer of the liquid immediately surrounding it, forming the so-called "Helmholtz Double Layer." The stability of hydrophobic colloids is determined by the potential difference between the particle and the surrounding film, but hydrophyllic colloids such as many of the proteins have sufficient attraction for water to remain in solution even when this potential difference is reduced to nothing. The hydrophyllic colloidal dispersions, unlike most of the hydrophobic ones, are of uniform particle size (the proteins having a molecular weight of 34,500 or a multiple of this) and many of their typical colloidal properties, such as swelling, viscosity and the potential difference between the particles and the solution can be accounted for quantitatively by the use of Donnan's theory of membrane equilibria. More recently this theory has been applied successfully to hydrophobic colloids by regarding the Helmholtz Double Layer and the external solution as the two phases.

In the last few years it has been shown that in the solid state, also, there is an orderly arrangement of the molecules, many even of the so-called amorphous substances possessing an orientated structure. Thus in animal and vegetable fibres as well as in the mineral ones there is a parallel packing of long molecules. In cellulose and silk these form long straight chains which slip over one another when stretched. In wool and rubber, however, these chains are spiral in shape and the great elasticity of these substances is due to the straightening of the molecules under tension.

COLOURING MATTER, NATURAL AND SYNTHETIC—*Joan E. Bull.* From the earliest times the production of colouring matter for various purposes has engaged the attention of man. Dyes were at first fugitive stains obtained from the juices of fruit, or decoctions from leaves, flowers, bark and roots, but gradually methods were discovered whereby the stain could be rendered permanent by the aid of certain earths containing iron and aluminium. Little advance was made until the discovery by W. H. Perkin in 1856 of the aniline dye, mauve. From then brilliant aniline dye-stuffs were rapidly produced and the artificial product supplanted the natural colouring substances.

Many theories have been put forward to account for the fact that an organic substance has the specific property of dyeing. It has been suggested that colour is due to close internal unsaturated linking between carbon, nitrogen or oxygen, whilst Witt suggested the necessity for certain definite groups of atoms to give the potentiality for colour, as well as a salt-forming radicle to bring out the colour and dyeing properties. It has also been shown that a system of conjugated double bonds produces colour, so that suitably substituted aromatic compounds are the main constituents of dyes.

Dyestuffs, from being classified into two simple divisions according as they were capable of being fixed with or without a mordant, are now classified into two large groups: (a) chemical class, consisting of fourteen subdivisions varying according to the chemical groups present, (b) dyeing class, of eight groups differing according to the method used to dye the article, but it was shown that no sharp line of division exists between these main groups.

The exact manner in which a dye unites with a fibre is indefinite. For wool and silk evidence favours equally the electrical, chemical and adsorption theories, whereas with the direct dyeing of cotton where affinity between fibre and colouring matter is feeble, the adsorption theory based on residual valencies in adsorbant and dye is the most satisfactory. Some, however, hold the view that the fibre exerts a purely physical attraction towards colouring matter and that the colour is held in an unchanged state by the fibre.

Whereas a very large number of dyes have been produced since Perkin's discovery, the number of new pigments made has been comparatively few. In 1928 there was discovered accidentally a new class of coloured organic compounds called phthalocyanins. The parent substance and its metallic derivatives are blue in colour and extremely stable. Synthesis has shown them to be built up of four isoindole rings joined by means of the extracyclic nitrogen atom, and the remaining valencies then form a conjugated chain in keeping with the strong colour.

The phthalocyanins bear a remarkable resemblance to the porphyrins being closely connected structurally with chlorophyll of plants and haemin of the blood. It is of interest to note that members of the porphyrin group have recently been isolated from oil-shale bitumen, from petroleum, asphalt and coals. It would indicate that in the future new colours showing a structural resemblance to many naturally occurring coloured substance may be synthesised.

COLLOIDS IN AGRICULTURE—*M. C. Franklin.* Recent years have seen a rapid increase in our knowledge of the fundamental changes underlying various phenomena which take place in soil processes, plant growth, and in the animal world and in these developments colloid chemistry has assisted us to understand more clearly many hitherto unexplained phenomena.

The extreme importance of both the inorganic and the organic colloid fractions of the soil are now thoroughly appreciated. Such phenomena as base exchange, the effects of different types of fertilisers, the mechanical composition of soils, the texture of the soil, its behaviour under cultivation by implements, and the way in which it responds to the sudden dictates of the weather are all being studied actively and explained by the colloid chemist.

It is now known that soil will exhibit cataphoretic phenomena, that such factors as water-holding capacity, change in volume, plasticity, cohesivity, flocculation and deflocculation properties are all conditioned by the percentage of colloidal material present.

Further, colloid science has assisted materially in explaining the soil development processes which take place under arid conditions, semi-arid conditions, or under humid conditions and has been of considerable assistance in mapping out and explaining such soil types as the White Alkali and Black Alkali Soils in the U.S.A., the black earths in Russia, podsol formation, and so on.

In the plant and animal world so overwhelmingly predominant is the part played by surface molecules in the chemistry of life processes that naturally one looks for reasons for the completeness of colloidal dominance. These follow from the necessity of the living cell to possess a high degree of permeability so that nutrients may enter readily from outside and so that waste products may be rapidly eliminated. Further, the plant or animal must possess sufficient rigidity to maintain its own individuality. The gel-like structure of plant and animal material permits these essentials to be fulfilled.

Starch, cellulose, proteins, enzymes, and many other substances occurring in living material all possess colloidal properties. Astbury's classical work on the structure of wool fibres and similar work by others has increased our understanding in very recent years of such phenomena as the elasticity of wool, wool shrinkage, and allied phenomena.

A knowledge of fundamental factors underlying smoke damage, plant protection by insecticides and fungicides has been increased considerably by a better understanding of colloid phenomena. For example, to quote Marshall, "Amongst the arsenical insecticides an assessment on the basis of arsenic content might be completely misleading. Particle size, which is a measure of covering power, and the choice of protective colloid, spreader, or adhesive are also of fundamental importance."

Other important phenomena in the plant world such as drought and frost resistance can be explained by the aid of colloid chemistry. Modern work suggests that water is present in the plant in two forms, "free" and "bound." Varieties of plants in which the "bound" form predominates are drought and frost resistant. The explanation of this difference between resistant and non-resistant varieties appears to be linked up with the gel nature of the protoplasmic material.

These are only a few examples in agriculture where the application of colloid principles have assisted the agriculturist towards a better appreciation and understanding of the intricate workings of Nature. The list could be enlarged considerably. Digestive processes in the alimentary canal, anabolic and katabolic changes in the animal body, milk, and numerous other processes or products fit more readily into the general scheme of things if colloid chemistry is called upon to assist in their explanation.

OTAGO.

Papers read—

Presidential Address.—*G. A. Holmes.*

"Chemical Aspects of Photography."—*J. W. Shields.*

"Joint Meeting with the Otago Branch of the Royal Society of New Zealand. Symposium on Milk."

"The Nature and Composition of Steel."—*R. M, Bruce.*

"The Chemistry of Tanning."—*H. Longbottom.*

"Current Researches in Chemistry."—*Honours and Research Students.*

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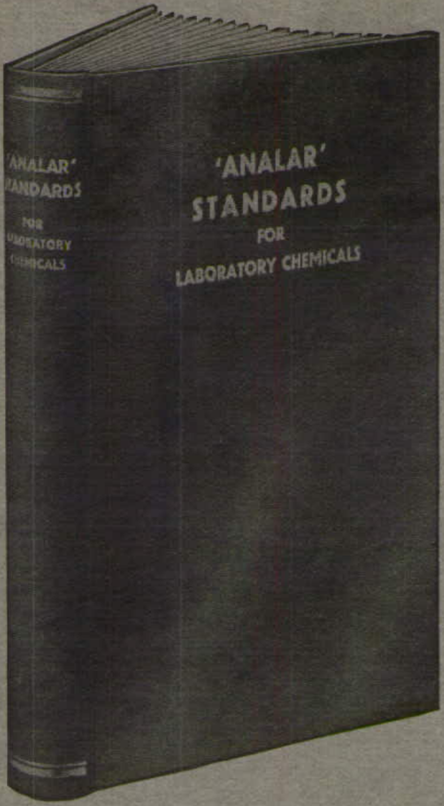

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