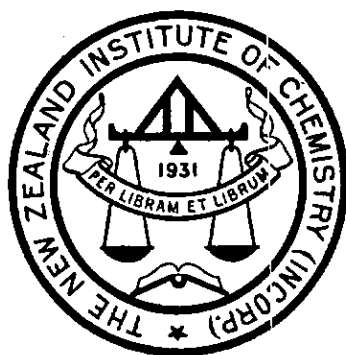


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The Coal Tar Industry in N.Z.

It's Achievements and Possibilities.

(By C. G. W. MASON, M.Sc., A.N.Z.I.C.)

Owing to limits of space, the original has been condensed and technical details omitted.

"The Gas Industry is one of the oldest, one of the best organised, and one of the most up-to-date of all the industries in the country. It has existed for about a hundred and thirty years, and the first gas company established here is still making progress and still flourishing. The industry was created for the manufacture of gas and that has always been the most important part, but the by-products have been found to be valuable and all the resources of engineering and chemistry have been applied to the recovery of these by-products and their conversion into substances valuable to mankind."

In these words, Dr. Stephen Miall, editor of "Chemistry and Industry," a dispassionate observer with keen perception and wide interests expresses his views on the gas industry and its relation to tar and other by-products in Great Britain.

To the gas engineer, coal tar is an incidental product to gas production, which has to be disposed of in the best manner possible under the circumstances existing. Tar can be an extremely embarrassing substance to dispose of, and was at one time a waste product, a veritable nuisance and embarrassment to the coal gas industry.

To the chemist, coal tar, that black, sticky, viscous fluid is one of the most romantic raw materials with which he can be privileged to work. What other substances can be made to yield by such a series of fundamental chemical and chemical engineering processes, so many unique compounds and valuable raw materials?

The sister material, petroleum, is undoubtedly not a "Cinderella" but this comparison serves only to increase the attraction of tar to the chemist in New Zealand. Not only does coal tar present such a varied source of absorbing problems, but it also provides one of the few examples of a true and comprehensive chemical industry in New Zealand: comprehensive because there is no other industry which requires a more extensive application of the principles of chemistry and chemical engineering.

Admittedly the application is on a comparatively small scale, but quantity of material handled does not influence the principles or chemical processes involved. The scale of operation does influence, however, the economic factors, thus making

the sound scientific application of the former principles of still greater importance.

Coal Tar may be defined as the mixture of condensable organic compounds produced during the heat treatment of coal. The physical and chemical characteristics of the tar are dependent on the following broad factors:—

1. Nature of coal—(a) Lignite, (b) Sub-Bituminous, (c) Bituminous, (d) Anthracite.

Tars produced from the carbonisation of the sub-bituminous and bituminous coals are the only ones to which consideration will be given.

2. Temperature and time of heating: (a) low, 400 to 800°C. (b) medium, 800 to 1000°C. (c) high, 1000 to 1500°C.

The time of carbonisation may vary in practice from six hours to twelve hours.

3. Type of retort and conditions of carbonisation:—The only type of tars which need to be considered are those produced from the high temperature carbonisation of bituminous coals in vertical or horizontal retorts.

The coal carbonised in New Zealand in 1938-39 was 226,265 tons, being 10.18% of the total coal mined.

The importance of the coal industry in New Zealand and the necessity of insuring the efficient utilisation of our coal resources, has been dealt with in detail from time to time, the most recent and authoritative Paper being "The Utilization of New Zealand Coal," by J. A. C. Bayne, F. W. J. Belton, and W. Donovan, N.Z. Journal of Science and Technology, Volume XIII, No. 6, Pages 353-70, 1932.

From crude tar, over 250 individual compounds have been isolated and identified. Relatively few of these are separated by the normal tar treatment works, but many narrow mixtures and pure substances are produced in large quantities for use as raw materials for other chemical industries.

The total estimated volume of crude tar produced is 2,500,000 gallons per year, and of this it is estimated that 85% is produced in the four main carbonising plants, namely, Auckland, Wellington, Christchurch and Dunedin.

It will be desirable to present a broad outline of the range of products obtained by the efficient treatment of Crude Tar. No attempt is made to give an exhaustive review of this aspect, but only to illustrate the range of products which are made in this country or which can reasonably be produced and utilised to economic advantage. The primary distillation of Crude Tar yields the following products:—

| | |
|-------------------|-------------------|
| Ammoniacal Liquor | Heavy Oil |
| Crude Naphtha | Crude Naphthalene |
| Middle Oil | Road Tar or Pitch |

The main object of the tar refinery is to separate these crude materials into refined products of maximum utility. The

range of products usually produced and their commercial uses are :—

| Primary Product | Product | Uses |
|-----------------------------|---|--|
| Ammoniacal Liquor | Ammonia Solution | Detergent Agent for Wool Washing, Household Ammonia, Fertiliser, Emulsion Production, Biological Culture Media Preparation. |
| | Anhydrous Ammonia | Refrigerant. |
| Crude Naphtha | Ammonia B.P. | Medicinal Requirements. |
| | Benzole | Motor Fuel, Solvent, Cleaning Fluid. |
| | Toluole | Constituent of Lacquers and Cellulose Solvents, Explosive Raw Material. |
| Middle Oil and Heavy Oil | Solvent Naphtha | Paint Vehicle, Polishes, Solvent for Rubber, Oils and Fats |
| | Resins | Paints, Thermo-plastic Resins |
| | Creosote | Disinfectant, Timber Preservative, Sheep Dips. |
| | Phenol | Pharmaceutical Requirements Synthetic Resins. |
| | Cresylic Acid | Disinfectants, Antiseptic Soaps, Synthetic Resins. |
| Naphthalene | Pyridine | Denaturant for Industrial Alcohol, Solvent. |
| | Horticultural Naphthalene | Soil Sterilisation. |
| | Sublimed Naphthalene | Moth Balls, Preservative for Rabbit & Sheep Skins, Furs, etc., for elimination of Moths and Weevils. |
| Road Tar | Light Tar Primer | Penetrating Coat for Roads. |
| | No. 1 British Standard Specification Tar | For Top-dressing and Sealing of Roads. |
| | No. 2 British Standard Specification Tar | For Tar Sealing. |
| Pitch | Soft Pitch | Preparation of Anti-corrosive Paints, Briquetting of Slack Coals, Coating for Preparation of Roofing Felts, Liquid Fuel. |
| | Medium Pitch | |
| | Hard Pitch | |

During the last critical years all of the foregoing materials have played some vital part in the country's war economy. There have been many occasions when the inadequacy of national production of coal products has been acutely apparent and regret has been expressed that operations are not on a very much greater scale.

That such a small proportion of total New Zealand Tar production is raised to the highest degree of economic utility is regrettable. The reason is to be found mainly in the fact that, whilst to the chemist, tar is a raw material of such wide possibilities, to the works manager of many of the smaller works, it is an embarrassing by-product. The controlling factor is, therefore, largely one of personnel, and it is for this reason that such a wide field has existed and a still wider one is awaiting the application of the knowledge and energy of the chemist.

Description of various portions of plant used in the distillation of crude tar and tar oils.

One type of tar still commonly used is a mild steel vessel 5 feet in diameter and 2 feet deep with a dished bottom and flanged cover fitted with tar inlet and vapour outlet pipes, safety valve and thermometer pocket. The still is mounted in a brick work setting and is heated by four gas burners consuming 1,200 to 1,400 cubic feet of gas per hour.

Before entering the still the tar passes through a regulating valve into a pre-heater where it is heated by the condensing distillate. The vapour outlet pipe connects to a vapour box where the heavy oil and a large proportion of the naphthalene are separated. The vapour then passes off to the tar pre-heater and condenses to yield crude naphtha and middle oil.

The crude tar flows into the centre of the still, the bottom of which is covered with molten lead. In this is placed a spiral labyrinth of four turns. This spiral dips below the surface of the lead, and is so placed that the tar flowing in at the centre makes four turns around the still over the molten lead before arriving at the distilled tar outlet. The depth of tar on the lead is approximately $\frac{3}{4}$ inch and the amount of tar in the still at any one time between three and five gallons. The quantity and quality of the products are governed by the temperature of the lead and the rate of tar flow. The dehydrated tar flowing from the still is conducted through a cast iron worm in a water cooler.

The cooled tar then flows to underground storage wells for blending and pumping to overhead steam heated delivery tanks for distribution. Insulated 400 gallon to 1000 gallon

tanker waggons charged from these overhead tanks distribute the tar to the spraying equipment for application to the roads. By this means tar can be distributed hot up to 100 miles radius from the works resulting in economy and efficiency of application.

Pitch Production.—When pitch is required the lead temperature is raised to 400°C. and the crude tar flow reduced to produce pitch of the required degree of hardness.

The Pitch is used for special anti-corrosive paint production, briquetting binder, and when blended in an appropriate manner and produced to a rigid specification, for the coating of paper felt for the production of roofing materials.

The tar is produced to British Standard Specifications No. 1 and No. 2, and light priming tar designated T.C.1 blended there from.

The contribution of these tars to New Zealand road surfacing requirements has been very considerable, and as has been the experience in Great Britain and Continental countries, tar to the appropriate specification produces roads highly satisfactory in performance and economical in production.

Detailed Treatment of Primary Tar Fractions.

The distillate is separated into three primary fractions: (a) Crude Naphtha, (b) Middle Oil, (c) Heavy Oil.

These fractions are treated individually for conversion to products so balanced that fractions of the highest value are obtained.

The Light Naphtha consists of the lower boiling range hydro-carbons boiling up to approximately 200°C. comprising benzole, toluole, solvent naphtha, and heavy naphtha. The crude naphtha is redistilled and separated into three fractions.

First Cut.—Usually made at 120°C. consisting of crude benzole and contains approximately 12% of toluole. Treatment of this fraction will be described in detail when benzole recovery is considered.

Second Cut.—Solvent naphtha is the fraction 120° to 170°C. This fraction is refined in a similar manner to the crude benzole.

Third Cut.—170° to 200°C. is used as a paint vehicle in the production of anticorrosive paints and other coating materials.

The Middle Oil fraction consists of the oils, boiling range 200° to 240°C. which, on cooling deposit a considerable amount of naphthalene. The oils, when cooled to atmospheric temperature are transferred to a refriger-

erating chamber where the temperature is reduced to 0°C. in twenty-four hours, thus depositing most of the remaining Naphthalene.

The refrigerated oils are then transferred to a storage well for subsequent removal of pyridine bases and tar acids, or alternatively, are used as such for blending with heavier creosote fractions for disinfectant production.

The Heavy Oils are either treated as described for middle oils or re-distilled for the production of British standard specification creosote oil for timber preservation; the distillate being blended with the middle oil fraction. Considerable flexibility is possible in the method of treatment outlined for these oils, narrower fractions being produced for special requirements such as sheep dips, gas washing oils, and tar blending oils for T.C.1 production.

For Tar Acid production the refrigerated oils containing 20 to 25% of total tar acids are transferred to a washer fitted with steam heating coils and stirrer. In this vessel the oils are washed with a 12% caustic soda solution, three washes being usually required for the complete removal of tar acids. The phenolate from the last wash is used for the first wash on the following batch of oil. By careful manipulation of ratio of soda to oil and reuse of phenolate the concentration of carbolic acid can be built up in the phenolate, and if it is required to produce this acid, the phenolate from this wash is kept separate. After soda washing the oils are treated with 40% sulphuric acid solution for removal of tar bases, this producing a neutral hydro-carbon oil which is blended with special tar acids for high grade disinfectant production. The phenolate is returned to the washer for treatment with benzole for the removal of entrained neutral oils. Two washes of 5% benzole are given; the phenolate is steam distilled with open and closed steam, until tests on the distillate show that sufficient neutral oils have been removed to produce acids of the required specification.

The next step is the carbonating of the phenolate. This is carried out by pumping the cooled liquor over a tower packed with "earthenware propellor" filling where it is carbonated.

Waste gas containing a high concentration of carbon dioxide is blown by means of a fan up this tower; sodium carbonate being produced and the tar acids separated in a special separating vessel. The acid layer is continually removed from the surface of the separator, washed with sulphuric acid to remove carbonate and water and then distilled in a special pot still.

The usual grade of acid produced is 97% pure cresols, but for special requirements B.P. cresylic acid has been produced.

The tar acids are mainly used for production of Lysol, disinfectants, soil sterilisers and for prevention of mould in leather processing. Certain soaps contain a small amount of tar acids, and they are used as an aid to dissolution in horticultural sprays with a petroleum oil base.

The use for soil sterilising is based upon the classic work of Sir John Russell, published in the Journal of the Society of Chemical Industry, Jubilee Number, 1931, Page 216, and entitled "The Action of Antiseptics in Increasing the Growth of Crops in Soil." It has been found that by appropriate treatment with antiseptics the bacterial content of soils can be balanced to result in greatly increased availability of plant food material with consequent improvement in early maturity and quantity of crop. This particularly applies to tomato production.

In the leather industry the tanned leather in its damp state is subject to mould deterioration and leather chemists have found that cresylic acid emulsion is an economical and effective material for elimination of this growth.

Disinfectants.

The large scale production of disinfectants in New Zealand commenced about 1920. Before this time they were imported from England to the extent of approximately £20,000 per annum. A number of attempts had been made to manufacture these materials on a large scale, but there was no reduction in the quantity imported until that year, after which there was a rapid decline until the importations practically ceased by 1938. The disinfectants manufactured in New Zealand are of equal efficiency and marketed at a considerably reduced price compared with the previously imported materials. The present consumption is estimated to be 60,000 gallons per annum.

The active ingredients of all coal tar disinfectants are the tar acids or phenols. These consist of phenol, or carbolic acid, the three isomeric cresols and the xylenols.

Of the phenols, only phenol itself is capable of use without special formulation. It was the first substance systematically used in disinfectants, and whilst it has maintained its usefulness to a considerable extent, it is being displaced by more strongly germicidal substances which do not have such a highly corrosive nature.

The low solubility in water of the cresols and the other tar acids necessitate special measures to give a dispersion of active ingredients in the medium to be disinfected.

By blending of creosote oils with tar acids the efficiency is enhanced so that for disinfectant production it is not usual

to separate the acids completely, but rather to reinforce the cresote if necessary by addition of suitable acids.

Commercial Disinfectants are of three main types, differentiated by the methods employed for compounding the active ingredients. These are: (a) black fluids; (b) white emulsions; (c) Lysol.

The black fluid type consists of a solution of high tar acid cresote oils in soap. The soaps used are produced from rosin or fatty oils saponified with potash or soda. Approximately 10% of water is present to render the mixture homogeneous and fluid. The requirements of a satisfactory material are:—

(1) It must emulsify spontaneously when poured into or diluted with water.

(2) When diluted it must have the power of killing micro-organisms.

(3) The fluid must be stable on storage and not subject to deposition of naphthalene or separation of water on cooling to the normal storage temperature.

(4) The dilute emulsion must be stable and show neither 'creaming' of the disperse phase nor separation of oily droplets.

(5) The formation of a white or cream emulsion is desirable with minimum tendency for development of pinkness on storage.

(6) The smell is required to be of such a nature that objectionable odours shall be masked, and be replaced by a 'clean' odour.

Tests are carried out to ensure that the material complies with the requirements of a good disinfectant. The most important of these tests is the determination of the Rideal-Walker Coefficient. This is the official test for germicidal efficiency and the standard technique for the determination is covered by British Standard Specification. The method consists of determining the concentration of the disinfectant which will kill the organism of a standard strain of *bacillus typhosus* in the same time as a standard pure phenol solution.

The Rideal-Walker coefficient is the number obtained when the dilution of the disinfectant is divided by the phenol dilution which shows no life after the same time of contact. Commercial black fluid type disinfectants normally have a coefficient of 3 to 4.

White disinfectants is the trade term for emulsified tar oils. This type of disinfectant is prepared by emulsifying 50 to 60% of selected tar oils in an aqueous continuous phase. A wide selection of emulsifying agents is available but there are few which, from all points of view, give completely satis-

factory results. The manufacture is fraught with all the difficulties usually associated with emulsion production, but with the modern advances in our knowledge of emulsions, a considerable degree of success is now achieved. The type of oil chosen has a predominating bearing upon the germicidal efficiency of the resultant fluid.

The mechanical operations during production of an emulsion of this type are as important as the chemical balance and the method of mixing has a considerable influence on the efficiency of emulsification. An important machine in achieving this is a homogeniser, which consists of a rotating disc travelling at 10,500 r.p.m. set at a distance of two thousandths of an inch from a stationary disc. The emulsion is pumped through this gap and a very fine state of subdivision of the disperse phase produced. The advantages of the emulsified type of disinfectant are, cheapness of production, and greater diversity of uses over the black soap solution type. The latter is not emulsifiable in salt solution or in the presence of urine, whilst the former can be mixed even with sea water and still retain its disinfectant powers. Actually this is not an important distinction for if the black type of disinfectant is pre-emulsified with pure water, dispersion in high salt concentrations is easily obtained. The ranges of oils which can be used, however, are more restricted than those suitable for black solutions and it is only certain producers who can manufacture this type.

Lysol type disinfectants are characterised by the fact that on adding to water a clear or slightly coloured solution and not an emulsion is produced. Lysol itself is prepared by dissolving B.P. cresylic acid in potash linseed oil soap.

The Rideal-Walker coefficient of these solutions is usually 2.5 to 3.5. For ordinary disinfectant purposes they are unnecessarily expensive, but for certain medicinal uses they are most desirable. A modern improvement is the substitution of chlorinated xylenols for the cresylic acid yielding a non-poisonous, non-irritant disinfectant of a superior type.

It is estimated that 400,000 gallons of disinfectant could be manufactured in New Zealand per annum, the only imported material required being caustic soda. The internal consumption is approximately 100,000 gallons per annum, so that the possibility of export to the South Pacific region is considerable.

Naphthalene Refining.

The crude naphthalene which separates from the primary distillates on cooling to atmospheric temperature, together with that from the refrigerated oils, is redistilled.

The fraction between 205°C. and 225°C. is collected separ-

ately, permitted to crystallise and then powdered in a disintegrator. Owing to the fact that powdering breaks the cell structure formed by the crystals, a large amount of the oil held in the lumps by capillary action is freed and drains away on storage of the naphthalene.

Final oil removal is obtained by centrifuging in a 'whizzey' and subsequent washing, whilst spinning, with benzole.

From the centrifuge the washed naphthalene is transferred to a subliming chamber.

Road Tars.

In view of the fact that in any tar treatment scheme the residual materials, road tar and pitch, form the bulk of the material handled, their avenue of disposal has an important bearing upon the economics of the industry.

Disposal as road tar has always been the main outlet and New Zealand produced tars have an important place in road construction. It is improbable that the quantity available would satisfy requirements so that the importation of bitumen will always be necessary. Both materials have their limitations and advantages.

Highways construction in New Zealand has received the attention of the Public Works Department engineers. In 1935, F. M. Hanson, M.M., delivered a paper before the N.Z. Society of Civil Engineers entitled "Bituminous Surface Treatment of Rural Highways." A comprehensive survey of the methods of road construction and the uses of various grades of tar and other bituminous materials is given. It is the work of the producers of road tar in New Zealand to supply materials to the specifications required by these large consumers.

With regard to the utilisation, Hanson, page 125, states "Tar can be treated to make all grades of bituminous roading materials, from thin low viscosity primer to heavy pitches for crack filling. When prepared to the correct grade and consistency, tar has no superior and probably not even an equal as a primer, and it is in this direction that the tar industry in New Zealand must look for much of its business. The tar manufacturers do not seem to realise the extent of this field which awaits development, nor do they seem to be making any strong efforts to investigate the possibility of using tar oils for fluxing or cutting back asphalts as is done in Australia."

Experiments have shown that for many purposes, tar is the better material. Since the above paper was written a considerable amount of work has been carried out in extending the use of tar for main highways construction, but this avenue

of utilisation still has far reaching possibilities. Hanson particularly recommends the use of tar blended with light oils to produce a tar primer or T.C.I. In regard to this, he states, page 126, "The future demand for road primers and other light tar products should be much greater than the No. 1 tar demand has ever been. As a road primer for "killing" dust, plugging the surface, and providing a thin bituminous skin to which a seal coat or any other thin surfacing will attach itself, asphalt or tar, cut back to the consistency of the M.C.I or T.C.I. specification respectively, probably have no equals. The high percentage of light distillates which these liquid bituminous materials contain, gives high penetration qualities and enables all particles of dust or fines to be coated or "killed." At the same time, a bituminous deposit develops, which seals and binds the surface. The penetration of somewhat dusty surfaces is rapid and complete, with the heavy bituminous material remaining in the upper layer of the road."

Pitch.

At present the market for pitch in New Zealand is strictly limited, not so much on account of the demand, but mainly because of the uneconomic price obtainable for briquetting. The more highly developed coal tar industry in Australia can, by recovering costs in the sale of oils and refined products, dispose of the pitch at a very low price. In fact, so profitable was the oil handling that the pitch could be dumped and the whole process show a working margin. Under these conditions locally produced materials could not compete.

A very promising use for a special grade of pitch was found during the first year of this war, as a coating material for roofing felt production. For this purpose bitumen is the standard material. This is not surprising in view of the fact that the industry works to American specifications. Shortage and high price of bitumen created a favourable opening for the introduction of coal tar pitch.

BENZOLE AND ALLIED PRODUCTS.

Benzole, toluole, xylene and solvent naphtha constitute an important range of products obtained from the lower boiling fractions of tar distillation. Owing to their high vapour pressures the amount remaining in the gas at atmospheric temperature is 25 times that separating with the tar, hence recovery from the gas is the important source of the crude benzole products.

Two methods of benzole recovery from coal gas are adopted:

- A. The oil washing process.
- B. The active carbon process.

The oil washing process is the oldest and most widely used method of benzole absorption from coal gas. This method depends upon the fact that when the gas is washed with a liquid hydrocarbon or mixture of hydrocarbons, that is not sufficiently volatile to vapourise in the gas, the vapours of the aromatic and other hydrocarbons in the gas dissolve in the oil, from which they can be removed by distillation. The absorbent oil, after cooling, can be re-used for washing the hydrocarbons from a further quantity of gas.

In addition to these vapours, other compounds such as carbon bisulphide, thiophene, traces of phenol and pyridine bases are simultaneously removed from the gas and appear as impurities in the crude benzole.

The process in outline consists of passing the "rich" gas containing the benzole vapours through one or more scrubbers, where it is washed with sufficient oil to recover effectively the benzole. The "benzolised oil" leaving the scrubbers is passed through a heat exchanger and a pre-heater whereby its temperature is raised to about 120°C. and some of the dissolved vapour is removed. The remainder of the benzole is recovered by the subsequent passage of the oil through a still provided with steam heated coils and a supply of open steam.

Debenzolised oil leaving the still passes through a heat exchanger, whence it gives up some of its heat to the cold incoming benzolised oil, thus effecting economy in the quantity of heat required in the process. Thence the oil passes through water coolers to the debenzolised storage tank. From here it is again pumped to the scrubber, and the cycle is repeated, the recovery process being continuous.

In the active carbon process, the purified coal gas is passed through active carbon contained in large cylindrical vessels until the carbon is saturated; when a change over to another carbon charged vessel is made and the benzole removed from the saturated carbon by means of steam.

As the benzole recoverable is largely present in the purified coal gas and the reduction in volume and heating value of the gas has to be replaced by increased coal throughout, the benzole recovery plant can be considered as a new gas consumer, which takes about 5% of the thermal output without extra sales and distribution charges. Furthermore, as the extraction plant can be placed in and out of commission at any time desired, latitude in meeting the extra gas demand is wider than that allowed for by a new actual gas customer.

The composition of benzoles extracted from the gas, and from the tar produced under the same conditions is practically the same. Benzole from the gas will, however, as is to be expected, contain a higher proportion of the lower boiling compounds than the benzole from tar.

The constituents of crude benzole may be classified into the following groups.

A. Saturated compounds—

- (1) Aromatic compounds.
- (2) Paraffins and naphthalenes.
- (3) Oxygen, nitrogen and sulphur compounds.

B. Unsaturated compounds.

C. Coloured compounds.

As previously discussed, the composition is subject to wide variation in composition in crudes from various works according mainly to the type of retorts and conditions of carbonisation.

Typical crude benzole from coal gas produced in New Zealand has the following distillation range:—

| Initial Boiling Point | 72°C. |
|---------------------------|-------|
| Up to 80°C | 2% |
| " " 85 | 15 |
| " " 90 | 45 |
| " " 95 | 61 |
| " " 100 | 71 |
| " " 120 | 85 |
| " " 140 | 91 |
| " " 160 | 94 |
| Specific gravity at 20°C. | 0.877 |

On refining this crude the following products and quantities are obtained:—

| | | |
|-------------------|-----|---------------------|
| Benzole | 80% | on refined products |
| Toluole | 10 | " " " " |
| Xylole | 1.5 | " " " " |
| Higher Homologues | 8.5 | " " " " |

The chemistry of the refining of benzole has been a subject of considerable investigation. Refining is carried out with the object of producing a product which complies with the following requirements:—

(1) Sufficient of the unsaturated hydrocarbons must be removed to prevent the formation of gumming material during storage or use.

(2) Corrosion producing substances must be removed, such as acidic or basic substances and sulphur.

(3) Combined sulphur in the form of carbon bisulphide and thiophene must be eliminated.

(4) Colour stability must be satisfactory.

(5) The refined material must not possess an unpleasant odour.

Owing to the fact that crude benzole generally contains hydrogen sulphide which produces, on storage, mercaptans and sulphur which are difficult to remove, the refining process is carried out as soon as possible after production.

Batch washes of 640 gallons of crude benzole are treated as follows:—

1st Wash: 5 gallons 10% caustic soda solution for hydrogen sulphide removal.

2nd Wash: 2 gallons sulphuric acid specific gravity 1.5 to remove bases.

3rd Wash: 2 gallons sulphuric acid specific gravity 1.7 for drying.

4th Wash: 1 gallon sulphuric acid specific gravity 1.84 for resinification of unsaturated hydrocarbons.

5th Wash: 2 gallons sulphuric acid specific gravity 1.84.

6th Wash: 4 gallons sulphuric acid specific gravity 1.84.

7th Wash: Copious water washes.

8th Wash: Repeat of 1st wash to neutralise.

9th Wash: Copious water wash.

The chemistry of benzole refining is an extremely complex process. Attempts have been made to devise a continuous refining process for moderate sized works, and a suitable plant for use under these conditions is at present being designed. If the extraction and refining process can be simplified for operation on gas works under the supervision of the staff available, there is every possibility that benzole extraction could be extensively undertaken in New Zealand. Whilst the quantity available would be only a small contribution to New Zealand's

fuel requirements the industrial uses for benzole and allied products are developing at such a rate that there is every indication that a large portion of the possible production could be used in industry. Toluole and xylole are valuable materials for solvents for cellulose lacquers, and there is likely to be a very considerable demand for these materials in the future. Furthermore, the synthesis of a wide range of chemicals with these substances as basic materials is a possibility of the future. For these reasons it is considered that every effort should be made to increase our benzole production.

FUTURE POSSIBILITIES.

This country is completely lacking in basic chemical industries, without which future industrial progress must be strictly limited. There are several industries of this type which must and will develop in the future, but in the coal tar industry we already have the raw materials, together with the demand for the products, which justifies development.

Of the many possibilities of the coal tar industry, space permits a treatment of only one—Plastics.

Of the total quantity of synthetic resin plastics produced in America in 1940 (amounting to 123,577 tons), 80.5% was produced from coal carbonisation products. As a fabrication material, plastic resins ranked fourth in importance after steel, copper and zinc, and their production exceeded that of aluminium. Subsequent demands have materially altered their relative importance and it is highly probable that, after the war, due to the rapid growth in production capacity, their utilisation will be considerably increased. The application of the results of fundamental research in order to yield products of material value to society, has always stimulated the popular press to draw far reaching generalisations on further extensions.

The interest of the "man in the street" in the strange and the new can be directed to create and encourage a healthy enquiring atmosphere. Electricity, photography, radio and aviation all passed through a phase during which the interest of the amateur and of the popular press found expression in the prediction of future possibilities. In due time the various developments fall into their proper place and become accepted normal parts of our existence, ceasing then to be of special interest to the lay mind.

At the present time the subject "Plastics" is passing through the phase in which public interest has been fired with the great developments which have been made, and has almost

run riot in predicting future possibilities. Whilst some of the possible applications of these versatile products of the research laboratory are yet no more than remote, it is necessary that an attempt be made to review the repercussions and potentialities of the coal carbonisation industry in New Zealand in this field.

There are a number of scientific workers in New Zealand who are taking an interest in plastics in their many aspects, and it is appropriate here to review briefly the possible extent of our resources. Firstly it can be stated that as the raw material for this production constitute a small portion of the products of coal treatment, the quantity available will depend upon the extent of the development of the coal carbonisation industry. Whilst the efficient utilisation of all the products of carbonisation must have a beneficial effect on the major industry, it would at present be uneconomic to set up an establishment, the primary object of which was to produce plastics from coal. Furthermore, although it is not impossible that in the future the production of materials for plastics manufacture may be the main object of a coal project it will be sounder to follow the lead of more highly industrialised countries in using the raw materials which are already available as incidental products of another major industry.

That New Zealand is in the future going to require a large quantity of plastics is undoubted. The high standard of living enjoyed by the people of this country makes the relative consumption of products of this type high. Also, the probable use of plastics in structural materials, and the urgent necessity for rapid and extensive developments in building after the war, makes it imperative that every avenue must be explored for their use in this direction. It cannot yet be said that plastics have been used on a large scale to facilitate house construction, or that their small scale use has been economically demonstrated. The advances in their production and use made under the stimulus of war conditions, their wide application in aeroplane fabrication and the manner in which laminated plastics have withstood the rigors of use as aeroplane propellers (and in some instances as ships propellers) appear to justify the prediction that satisfactory structural stability could be achieved for house construction.

If a synthetic resin industry were developed in New Zealand, it is highly probable that economic success would be better assured if the available resources were used for the mass production of standard types of resin suitable for use in a large uniform market such as that offered in house construction.

Whilst it may be considered more advantageous economically to use the material available for the manufacture of products commanding the highest price, and use any surplus for

products which are of a lower value, it is necessary to take into consideration the much higher degree of refining required to produce the high grade resins.

Further, the technical skill and the expensive and complicated plant required for the production of a wide range of high priced articles, would probably not be justified by the market available.

For the successful production of laminated building sheets using synthetic resins for bonding the layers, a greater degree of latitude is permissible in the purity of the major constituents. This does not mean that any less care can be allowed in the preparation, but that production on the larger scale thus made possible will make standardisation more economically achieved, and this is a factor of major importance in the early success of a synthetic resin industry based on New Zealand produced materials.

This is exemplified by the fact that the synthetic resin chemist prefers to work with pure raw materials for high class products. Now it must be stressed that our production will be on a comparatively small scale due to the limited raw materials available and the fine separation of the mixed phenol, cresols and xylenols would in all probability necessitate plants of capacity below the economic unit. The "economic unit" is defined as a plant of such size that any increase in its capacity would not yield any significant decrease in the unit cost of the product. Unfortunately the relatively small scale of almost any chemical industry in this country makes this factor of primary significance in any project, and particularly so in synthetic resin production. For this reason accurate estimates of the quantities of raw material available and the finished products possible become of first importance.

Estimate of the Quantity of Coal Tar Synthetic Resins which could be produced from the Raw Materials available.

The treatment of chemical products from coal carbonisation has developed sufficiently to permit a reasonable calculation of potential production. Whilst in some instances the estimates are sufficiently accurate for defining the limits of a project, in other cases they may provide a foundation and guide for more detailed investigation. The output from the largest carbonising works (excluding the Waikato Carbonisation Co. Ltd) is taken, since it is considered that in the majority of other cases the size or location is such that recovery would be uneconomic.

Crude Tar: The total volume of crude tar produced by the six largest coal carbonising works in 1943 is estimated to be 2,140,000 gallons.

Total Crude Tar Acids: Making due allowance for the different types of tar produced from coal carbonised in vertical and horizontal retorts, the crude tar acids are estimated to be 153,000 gallons. Allowing conversion of 80% to refined acids this figure becomes 123,000 gallons.

Naphthalene: Production is estimated to be 574 tons of crude, yielding on purifying, 460 tons of refined naphthalene.

Benzole and Naphtha:

| | |
|----------------------|-----------------------------|
| Recoverable from tar | 70,000 gallons |
| Recoverable from gas | 500,000 gallons |
| Total | <hr/> 570,000 gallons <hr/> |

Allowing a refining loss of 20%, yield is 456,000 gallons
Comprising—

| | |
|------------------|-----------------|
| Benzole | 360,000 gallons |
| Toluole | 45,000 gallons |
| Xylole | 5,000 gallons |
| Naphtha | 46,000 gallons |
| Coumarone resins | 26 tons |

Ammonia: Although not recoverable in large quantities from crude tar, ammonia forms an important raw material for synthetics and is recovered in New Zealand entirely from the products of coal carbonisation. Estimated possible production is 450,000 lbs. per annum.

Formaldehyde: Whilst formaldehyde is not produced direct by coal carbonisation, its main source is from coke via the water gas reaction, a standard gas works process. The quantity which could be produced is in excess of the probable demand, the limiting factor in commercial production being the approximation of the demand to the "economic unit."

The Quantities of Plastics which could be produced from the available raw materials.

As already stated potential productions are extremely difficult to estimate and whilst the figures for essential raw materials are based on reliable figures, factors for their conversion to finished plastics are subject to considerable variation. Accurate information on details of manufacturing processes abroad, particularly in respect to refining losses, is at present

scanty. Whilst there are good grounds for anticipating that this information will in the future be available, it is hoped that some useful purpose will be served by presenting estimates based on present available facts.

The limited space of the present review does not permit a detailed statement of data; but it is felt that a statement of the extent of production possibilities might fulfil a useful purpose in placing possibilities in their right perspective.

Estimated acids available for plastics production = 1,000,000 lbs. In parts by weight 100 parts acids + 90 parts 37% formaldehyde + 30 parts 20% ammonia, yield 105 parts of phenolic resin. 1,000,000 lbs. acids = 446.4 tons; hence 446 tons acid + 148.5 tons formaldehyde + 26.76 tons ammonia = 468.3 tons resin.

Phenol by synthesis from benzene: 360,000 gallons of benzole yield 300,000 gallons of benzene. In phenol synthesis 100 parts benzene yield 110 parts phenol, hence 300,000 gallons (= 1178.5 tons benzene) yield 1,296 tons phenol. On transforming to synthetic resin this will yield 1,339 tons phenolic resin. Therefore total estimated quantity of phenolic resin per annum = 1,807 tons.

Required for its production is formaldehyde, 601.7 tons; Ammonia, 113.5 tons.

(Of the 96,000,000 lbs. phenol used for synthetic resin in U.S.A. in 1940, 72,000,000 lbs. were produced synthetically from benzene.

It must be stressed that it is assumed that all the available raw materials are diverted to this end.

Resins based on naphthalene: Naphthalene yields by oxidation, phthalic anhydride, which by conjunction with glycerine, produces the glyptal resinoids, and with methyl, ethyl or butyl alcohol yields the corresponding phthalates, which are the most commonly used resin plasticisers.

460 tons of naphthalene is estimated to yield 426 tons of phthalic anhydride. (Conversion of naphthalene to phthalic anhydride and efficiency figures see "Catalytic Oxidation of Organic Compounds in Vapour Phase," Marek & Hahn).

Coumarone indene resins: These resins are produced during the refining of benzene and naphtha, being left as a residue from the distillation of the benzole, after washing with sulphuric acid. These valuable resins are the easiest to make, and a certain amount has already been produced in this country. Estimated total amount producible is 26 tons per year.

Many other types of synthetic resins are made from the

products of coal carbonisation; but it is not the present object to cover all phases of resin production.

It can be confidently predicted that the gas industry can, by appropriate organisation, meet many of the synthetic resin requirements of this country. The setting up of a special plant with the primary object of treating coal specially to produce synthetic resins would certainly not be economic; and cannot be justified when so much of the material already available could be diverted to this important end. The future of the coal carbonisation industry in New Zealand will hold many attractions for the chemist, and presents possibilities for the development of a major chemical industry.

