

PRESENTLY LITTLE-USED BUT POTENTIALLY IMPORTANT
COAL TAR CHEMICALS

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To date, about 400 of the myriad substances contained in coal tar have been definitely identified. This figure may seem small compared to the 10,000 estimated to be in tar but it probably includes all the components that will be used commercially as such since some of the constituents are present in extremely small amounts. The compounds which have been identified are either those which are present in the largest amounts or those which are relatively easy to isolate. It should be remembered that the composition of the lower boiling fractions is more completely understood than is that of the higher boiling fractions and of coal tar pitch--the distillation residue.

The composition of coal tar varies greatly. It is influenced by the type of coking coal employed, by the coking process and by the coking temperature. Further, tar undergoes certain changes in composition on distillation and the yield of various constituents is influenced by the distillation process used.

The development of gas chromatography has greatly facilitated the quantitative determination of coal tar constituents. It proved to be an almost ideal method of investigating tar and its fractions, and has generally superseded other analytical methods that were less accurate and more tedious. The following quantitative data on the occurrence of compounds in coal tar were largely obtained with the aid of gas chromatography. It should be noted that these data relate to high-temperature tar from soft coal of the Ruhr area processed by continuous vacuum distillation.

Figure 1 is a gas chromatogram of such tar. The individual peaks represent the most important constituents from indene (boiling point at one atmosphere: 183.1°C) to coronene (boiling point at one atmosphere: 525°C) in the order of their boiling ranges. As this is a schematic diagram covering the whole tar, not all the quantitatively important compounds are indicated by separate peaks. For instance, the peaks of 1- and 2-methylnaphthalene and also those of phenanthrene and anthracene coincide. A more detailed gas chromatographical analysis of the tar would separate these isomers. However, since gas chromatograms become less easily followed as the number of peaks increases, further diagrams will not be shown.

All together, the compounds identified to date make up about 55 per cent of the tar. In addition, tar contains about 2 per cent of relatively high-molecular-weight, soot-like compounds that cannot be dissolved or distilled--making it impossible to determine their composition by chemical methods. Thus it is apparent that only a small per cent of the number of compounds believed to be present in coal tar have been identified; those that have been identified represent a very significant portion of the tar.

According to present knowledge, a maximum of eleven compounds occur in coal tar in proportions greater than 1 per cent. Excepting the two methylnaphthalenes, all of them are unsubstituted, aromatic substances without functional groups. The three compounds present in the largest proportions are a binuclear, a trinuclear, and a quadrinuclear hydrocarbon.

Table I
Compounds Present in Coal Tar in Amounts
Greater Than 1 Per Cent

<u>Compound</u>	<u>Per Cent</u>
Naphthalene	10
Phenanthrene	5
Fluoranthene	3.3
Pyrene	2.1
Fluorene	2.0
Chrysene	2.0
Anthracene	1.8
Carbazole	1.5
2-Methylnaphthalene	1.4
Dibenzofuran	1.0
1-Methylnaphthalene	1.0

Until quite recently coal tar has been the only source of aromatic compounds. The slight extent to which this source has been exploited, however, is not widely known. Of the eleven most abundant constituents of coal tar, only two--naphthalene and anthracene--are being used on large scale as pure products for chemical processes. Contrasted with naphthalene, almost all of which is recovered and further processed, anthracene is used only to a limited extent in the chemical industry, although the amount has increased recently. This paper is not concerned, however, with compounds now used technically on a relatively large scale, but with the still untapped possibilities of coal tar. What coal tar constituents have been used widely in their pure form? Compared to the potential, the number is extremely small: besides naphthalene and anthracene, the list includes only phenol and its homologs (cresols and xylenols); pyridine and its homologs; and quinoline. With both phenol and pyridine homologs, mixtures and not pure products are frequently used. Nevertheless, it should not be concluded that little attempt has been made over the years to exploit the chemical potentiality of tar.

Most organic industrial processes for the manufacture of synthetic fibers, resins, pesticides, dyestuffs, drugs, etc. employ small, reactive building blocks from which the end products are synthesized. When coal tar components are small and reactive, as phenol and the pyridine bases, they meet these requirements and are used. But most of the compounds present in coal tar have relatively large molecules without functional groups and are quite inert chemically. This is why--what seems surprising at first glance--of the eleven most abundant constituents of coal tar, only two find wide application. Naphthalene, the chief constituent, is a noteworthy exception among the tar aromatics. It has become a valuable raw material because, fortunately, it can be oxidized in high yield to phthalic anhydride.

Conditions may seem less favorable when we consider the other aromatics, but it nevertheless would seem advisable to investigate the various possibilities offered by these raw materials which are available in such quantity. Certainly in recent years remarkable progress has been made in recovery techniques, so that today most of the products are available in purer grades and at lower prices than a few

years ago. Although this has led to a gratifying increase in sales, there is still no realistic comparison between the demand for most products and the quantities that could be produced.

Phenanthrene

Phenanthrene, the second largest constituent of coal tar, still has not been used to any appreciable extent though the phenanthrene skeleton underlies multitudinous hydroaromatic compounds widely distributed in nature and having great physiological significance. These natural products include: resin acids, morphine, sterols, bile acids, digitalis glycosides, sex hormones, and antirachitic vitamins.

There is an extensive literature on the chemical reactions of phenanthrene--such as halogenation, nitration, sulfonation, alkylation, chloromethylation, metalization, hydrogenation, and oxidation--with numerous uses proposed for the reaction products. Uses such as in the manufacture of resins, dyestuffs, drugs, plasticizers, and--as solid chlorination products--nonflammable electrical insulators and impregnants.

About 10 million tons of crude tar are distilled annually in the Western World. Assuming that this entire output has the same phenanthrene content as coal tar from the Ruhr area, or 5 per cent, and that about half of the phenanthrene could be recovered, the impressive quantity of 250,000 tons of phenanthrene yearly would be available. Separation on a large scale would, of course, result in lower production costs. Since phenanthrene has a higher boiling point than naphthalene and because it is more difficult to recover, it will always be more expensive, but if produced on the same scale as naphthalene, its price would be much lower than it is at the present time.

By analogy to naphthalene, it may be expected that phenanthrene can be oxidized to produce a bivalent acid, diphenic acid, which if cheap enough could be used in the manufacture of synthetic resins and plasticizers.

Diphenic acid is already being produced from phenanthrene, but so far there has been no success in developing a simple commercial process with a high yield for the conversion of phenanthrene into diphenic acid or its anhydride. The process currently followed gives not only diphenic acid but also considerable amounts of other oxidation products. Because of the poor yield and trouble with subsequent purification, diphenic acid is currently priced so high that it is used only for specialized purposes. However, much research is going into the problem, so there are good prospects that an economic process will be developed before long. As soon as one application of phenanthrene gains industrial importance, the price reduction will open up additional markets where phenanthrene has been unable to compete for price reasons.

Fluoranthene

While it is well known that large amounts of phenanthrene are available from coal tar, we seem to be less prone to realize that next to naphthalene and phenanthrene, fluoranthene is the most abundant coal tar constituent. Assuming the

conditions described for phenanthrene recovery, fluoranthene is available in the amount of 165,000 tons yearly as a raw material. The fact that organic chemistry treatises frequently ignore fluoranthene entirely or mention it only in marginal notes, shows how neglected the compound has been. Nevertheless, fluoranthene has an advantage over phenanthrene since, like naphthalene, it can be readily obtained from the appropriate fraction in a high purity, because the fluoranthene fraction has no significant content of material less soluble than fluoranthene or which forms mixed crystals with it.

Thus fluoranthene is offered in technical grade in a purity of 97-98%. As with phenanthrene, mass production could reduce its price considerably.

Coal tar is now usually processed by continuous distillation. The fractions recovered, in the order of their boiling ranges, are: water, light oil, middle oil (carbolic oil), naphthalene oil, wash oil, low-boiling anthracene oil, high-boiling anthracene oil, and pitch (distillation residue). Other closely cut distillate fractions yielding concentrates of other main constituents could be separated in the same way as the naphthalene fraction in the primary distillation. However, since the largest part of coal tar distillate is used as creosote, a broad complicated mixture of compounds, this type of distillation is not profitable or generally practiced.

Fluoranthene is a constituent of the high-boiling anthracene oil, and to a lesser extent of the pitch. To obtain the fluoranthene fraction, the high-boiling anthracene oil must be distilled further. This yields a number of other fractions, the most important one being the pyrene (boiling points at one atmosphere: pyrene, 393°C; fluoranthene, 383.5°C). Fluoranthene costs would be much lower if the pyrene fraction could also be used instead of being returned to the high boiling anthracene oil. (The co-product problem becomes more complex and important as the amount of the desired material in the tar becomes less. In practice, only the two most abundant constituents, naphthalene and phenanthrene, are free of this burden).

Compared to phenanthrene, the literature on the chemical reactions of fluoranthene is limited. Halogenation, nitration, sulfonation, hydrogenation, oxidation, and condensation with phthalic anhydride and acid chlorides are reported. Despite the symmetry of its molecule, fluoranthene is not chemically inert! Since fluoranthene is readily accessible in a high purity and is relatively reactive, why has it had no important practical application to date? Probably because the compound failed to attract the attention of chemists in the past and since the ease of its recovery was not fully appreciated. An examination of its reactions suggests fluoranthene could perhaps be used as a starting point for the synthesis of drugs and particularly of dyestuffs.

The price of fluoranthene would be the determining factor in the commercialization of any dye derived from it and the price could be reduced only if a certain minimum sales outlet were assured. As far as we know at the present time the oxidation type reactions are not as promising as with naphthalene or phenanthrene because no novel multicarboxylic acids have been made from it.

Pyrene

Unlike phenanthrene and fluoranthene, pyrene is already being used as a raw material on a very modest scale compared to the potential 100,000 tons a year which is available. The chemistry of pyrene has been extensively investigated (halogenation, nitration, hydrogenation, oxidation, sulfonation, condensation, etc.) A large number of condensation reactions have been reported and deserve special mention. These include not only condensation with phthalic anhydride but also with acetic anhydride, benzoyl chloride, diazoacetic ester, dichlorodiphenylmethane, glycerin, cyanuric chloride, and formylmethylaniline.

The possibility of combining the production of fluoranthene and pyrene (boiling points at one atmosphere: fluoranthene, 383.5°C; pyrene, 393.5°C) has already been discussed under fluoranthene. As in the case of fluoranthene, pyrene is found in both the high-boiling anthracene oil and pitch. However, recovery of pyrene is more complicated because its fraction has some slightly soluble components boiling close to pyrene, including 1,2-benzodiphenylene oxide and 2,3-benzodiphenylene oxide. These are troublesome and expensive to remove. This explains the fact that pyrene is not ordinarily offered in as high a purity as fluoranthene. The technical grades available have a pyrene content of only 90-95%.

It is difficult to forecast if pyrene, so far used mainly as a starting material for the synthesis of dyestuffs, will become important in other fields. With successful utilization of fluoranthene as a chemical raw material, the market outlook for pyrene would undoubtedly improve. Many possibilities for its use are currently barred by its high price. Even if pyrene and fluoranthene recovery are combined, however, pyrene production costs would be reduced only slightly because, as previously mentioned, it is harder to upgrade the pyrene fraction than the fluoranthene fraction.

Like phenanthrene, there are interesting oxidation products of pyrene, such as 4,5-phenanthrenedicarboxylic acid and 1,4,5,8-naphthalenetetracarboxylic acid.

Naphthalenetetracarboxylic acid would be a particularly promising pyrene derivative if there were a simple oxidation process available giving a high yield of the acid. Experiments directed to this end have not yet given reason for optimism.

Fluorene

Wash oil boils between 230°C and 300°C; fluorene, occurring in tar in about the same proportion as pyrene, has the highest boiling point of main constituents in this fraction. Acenaphthene and dibenzofuran (diphenylene oxide) boil slightly below fluorene (boiling points at one atmosphere: acenaphthene, 278.2°C; dibenzofuran, 285.1°C; fluorene, 297.9°C). It is, therefore, convenient to consider the three together. However, fluorene and dibenzofuran must be carefully separated by distillation because they form a continuous series of solid solutions which, of course, cannot be separated by crystallization techniques.

Formation of mixed crystals is common among the constituents of coal tar. Phenanthrene and anthracene, phenanthrene and carbazole, and chrysene and 1,2-

benzanthracene are other quantitatively important compounds which form a continuous series of mixed crystals characterized by a curve having no maximum or minimum between the freezing points of the pure components. The formation of mixed crystals between phenanthrene, anthracene and carbazole is the main reason that phenanthrene is more difficult to purify than naphthalene.

Fluorene is the first of the coal tar constituents discussed so far to have a reactive group: in this case the methylene group between the two benzene rings has highly reactive hydrogen atoms. In spite of numerous reactions described in the literature and numerous uses suggested, such as the manufacture of cleaning and wetting agents, textile auxiliaries, pharmaceuticals, disinfectants, pesticides, dyestuffs, liquid scintillators, and thermoplastic resins, all attempts to promote widescale development of fluorene as a chemical raw material have been unfruitful to date. Recent developments indicate that there may be an outlet in drug synthesis because pharmacological substances currently being tested have been obtained from fluorenone, a product readily prepared from fluorene.

Chrysene

Chrysene, the most abundant constituent of coal tar pitch, is also found in smaller amounts in high-boiling anthracene oil. Because of a high-boiling point (440.7°C at one atmosphere) and the extraordinarily high-melting point (255°C), the product is hard to recover in its pure form. The starting point for chrysene production is usually the distillate from the manufacture of hard pitch, though pitch coke oil from the coking of hard pitch is also rich in chrysene.

Provided that suitable applications can be found, there seems to be no reason why all of the compounds discussed up to this point should not be used on large scale industrially. There is, however, less chance for chrysene despite the fact that its occurrence in coal tar is about the same as that of fluorene and pyrene. Purification of chrysene is more difficult and the higher cost of the compound will be a serious handicap to its broad utilization. Chrysene derivatives have been used to some extent in ultraviolet filters and sensitizers.

Carbazole

Carbazole, quantitatively the most important heterocyclic constituent of tar was, until recently, sold in large quantities. It is recovered as a co-product in anthracene purification. It was used for the production of dyestuffs and pesticides.

When fused with polysulfide in butanol or roasted with polysulfide in the presence of organic bases such as benzidine, the 3-(4'-hydroxyphenyl)-aminocarbazoles obtained by the condensation of carbazole with p-nitrosophenol yield the sulfur dye-stuff, hydron blue R, or when N-ethylcarbazole is employed, hydron blue G. 2-Hydroxycarbazole-3-carboxylic-acid-p-chloroanilide has become familiar as the brown dyestuff, naphthol AS-LB. 1,3,6,8-Tetranitrocarbazole became important as an insecticide under the trade name, Nirozan.

Finally, through the production of poly-N-vinylcarbazole a plastic has been developed from carbazole having good dielectric properties, good chemical resistance, high softening point, and thermal stability. This product has found commercial use in the electrical industry (trade names for polyvinylcarbazole: Luvican and Pollectron).

Unfortunately, the use of all these interesting derivatives has declined considerably in recent years, and some manufacturers of dyestuffs now specify that the anthracene material supplied to them contain less than a certain amount of carbazole.

A prognosis of the market for carbazole is, therefore, difficult. There is reason for certain optimism about the future of carbazole because it is a co-product in the production of anthracene and it does have a number of significant uses. Nevertheless, carbazole sales can be restored only with the development of new uses.

1-Methylnaphthalene/2-Methylnaphthalene

The two monomethylnaphthalenes are present in tar in very considerable amounts, with 2-methylnaphthalene predominant. In high-temperature tar, the ratio of naphthalene to the monomethylnaphthalenes is about 4:1, the lower the coking temperature, the more this ratio shifts in favor of the methyl- and dimethylnaphthalenes.

The methylnaphthalene fraction is a constituent of the "wash oil". It is distilled after the naphthalene fraction before diphenyl and the dimethylnaphthalenes. Methylnaphthalene production, therefore, fits nicely into recovery of the other three.

Because of their ready accessibility the methylnaphthalenes have become more important recently, even though the quantities sold are still very limited. Many possible uses have been proposed for each isomer; but these frequently overlap uses for naphthalene. Since naphthalene is cheaper, it has an advantage over the monomethylnaphthalenes in these cases. The syntheses of 1-naphthylacetic acid serves to illustrate such competition between naphthalene and 1-methylnaphthalene. 1-Naphthylacetic acid, used as a growth promoter, can be made from 1-methylnaphthalene by chlorination, reaction with KCN and subsequent hydrolysis. It can also be made by the chloromethylation of naphthalene followed by the same reactions. The synthesis selected then becomes a matter of cost.

1-Methylnaphthalene has an unusually low freezing point (-30.6°C) which is lowered further in the technical grade by the presence of isomeric 2-methylnaphthalene. Because of this property and its high solvent power, the alpha isomer is used as a solvent and as a heat transfer oil. It can also be used as a carrier in the dyeing of polyester fibers, as a cetane-number indicator. It has been used for determining the theoretical number of trays in distillation columns. Other suggestions for use are as an extraction agent for sulfur, as a constituent of liquid dielectrics, and as a starting material in the manufacture of plasticizers, pesticides, plastics, and textile auxiliaries. However, these suggestions have not been developed to any significant extent.

The numerous uses which have been proposed for 2-methylnaphthalene, include the production of dyestuffs, textile auxiliaries, growth inhibitors, detergents, emulsifiers, and wetting agents. The beta isomer is of importance in that its 1,4-quinone is a starting product for the manufacture of Vitamin K.

Dibenzofuran (Diphenylene Oxide)

Dibenzofuran is the most abundant oxygen heterocyclic compound in coal tar. The analogy in composition and occurrence between dibenzofuran and carbazole, the most important nitrogen heterocyclic, is striking. The presence of dibenzofuran in the wash oil and the advantages of combining its production with that of fluorene and acenaphthene have already been discussed.

Dibenzofuran is the skeletal substance of morphine. The reactions of dibenzofuran (halogenation, nitration, sulfonation, methylation, hydrogenation, and condensation) are reported in the literature. Possible uses are also described, such as the manufacture of disinfectants, insecticides, wood and other types of preservatives, textile auxiliaries, synthetic resins, high-temperature lubricants, dyestuffs, and additives for candle mixes. Dibenzofuran has been used to some extent as a dyestuff intermediate. Because of its high thermal stability, the product is suitable for heat transfer media although its high melting point (+82°C) is an objection.

An interesting derivative of dibenzofuran is o,o'-biphenol (2,2'-dihydroxydiphenyl), obtained by fusion with caustic potash. This compound is used in the manufacture of disinfectants and pesticides.

Acenaphthene

The acenaphthene content of crude tar is about 0.5%. However, larger quantities may be found in coal tar distillates because acenaphthene is one of those few compounds which may be formed in tar during distillation. The amount formed in this way may be equal to that originally present and the net acenaphthene content of coal tar is about 1%, roughly the same as dibenzofuran. Like fluoranthene it is easily purified by crystallization of the appropriate distillation fraction and the technical grade is usually 97-98% pure.

The chemical reactions which result in the production of secondary acenaphthene are not completely understood. The most likely reaction would be the dehydrogenation of 1,8-dimethylnaphthalene but since this cannot be demonstrated quantitatively, it must be assumed that there are other compounds in coal tar which are converted to acenaphthene by heat.

Like pyrene, acenaphthene belongs to the class of aromatics that have been used as starting materials for dyestuffs, but on a scale which consumes only a fraction of that which could be produced.

By means of catalytic gas-phase dehydrogenation, acenaphthene can be converted to acenaphthylene, which can be easily polymerized with peroxide catalysts. Like co-polymers containing acenaphthylene, the polyacenaphthylenes are noted

chiefly for their good electrical properties and high melting points but have not yet attained practical importance. A high yield of naphthalic anhydride is obtained from acenaphthene by catalytic gas-phase oxidation. Naphthalic anhydride has been used chiefly in the manufacture of dyestuffs. At a lower price it could probably be used for the production of synthetic resins.

On the whole, the market outlook for acenaphthene is more favorable than for its two by-products, dibenzofuran and fluorene. To reduce production costs as far as possible, effort must be concentrated on finding uses for substantial quantities of all three compounds.

Indene

Indene, the lowest-boiling of the most abundant coal tar constituents, is the reverse of acenaphthene so far as recoverability is concerned. The primary indene content of tar is almost 1 per cent. But in counter-distinction to acenaphthene, the amount of which increases during distillation, the amount of indene is decreased because at high temperatures and in the presence of hydrogen it is easily converted into indan. The extent to which the indene content is reduced and indan formed depends on the type of distillation process; the longer and higher the temperature at which the tar containing indene is heated, the greater the reduction of indene content. Under unfavorable conditions, more than 50 per cent of the original indene content of the tar may be lost. Since indene is more valuable than indan because of its higher reactivity, the hydrogenation of indene is an extremely undesirable reaction.

Indene cannot be classed as one of those coal tar constituents which has no practical use at this time even though it is not isolated and used as such. Indene is the principal constituent of coumarone resins. These would more accurately be called indene resins.

Because of its relatively high freezing point--(-1.6°C) pure indene can be prepared from the appropriate distillation fraction by extreme cooling. However, in spite of the many uses proposed for it, pure indene is not important commercially.

In addition to the large volume constituents of coal tar so far discussed, there are many other materials available in reasonably large amounts, which likewise have not attained commercial significance. The most important of these appear in the following table.

Table II
Important Coal Tar Constituents

<u>Compound</u>	<u>Content of Coal Tar (Per Cent)</u>
Diphenyl	0.4
Indole	0.2
2-Phenylnaphthalene	0.3
Isoquinoline	0.2
Quinaldine	0.2
Acridine	0.6
Phenanthridine	0.2
7,8-Benzoquinoline	0.2
Thianaphthene	0.3
Diphenylene Sulphide	0.3

Diphenyl

The diphenyl-indole fraction occurs between the methyl- and dimethylnaphthalene fractions. Recovery of diphenyl and indole is conveniently combined with the methylnaphthalenes.

Diphenyl is well known as a constituent of heat transfer oils. The eutectic mixture of diphenyl and diphenyloxide is sold under the trade names "Dowtherm A" and "Diphyl".

Diphenyl is also used as a preservative; for example, citrus fruit wrappers are frequently impregnated with diphenyl. It should be mentioned too that diphenyl is the basic substance of the benzidine dyestuffs, though they are normally produced from other starting materials.

Contrasted with what could be produced, very little coal tar diphenyl is used commercially. Coal tar diphenyl is under a handicap because diphenyl is available from other sources. It is obtained as a by-product in the synthesis of phenol by the chlorination process and it can be made by the pyrolysis of benzene. The diphenyl market, therefore, is divided between that recovered from coal tar and that made synthetically.

Indole

Indole, the nitrogen analog of indene, is one of the most interesting constituents of coal tar. Separation of indole and diphenyl is not possible by simple distillation because the two compounds have vapor pressure curves which lie close together and also form an azeotropic mixture. The boiling point of the diphenyl-indole azeotrope is a few degrees lower than the pure products (boiling points at one atmosphere: indole, 254.7°C; diphenyl, 255.6°C). Separation of indole and diphenyl is achieved by taking advantage of the slight acidity of the imide group and isolating the indole from the diphenyl fraction via its potassium compound by fusion with caustic potash. Diphenyl then can be recovered from the indole-free oil by fractionation and crystallization.

Another method of separating the two compounds is by the addition of a third component, diethylene glycol. Azeotropic mixtures of diphenyl-diethylene glycol and indole-diethylene glycol boil twelve degrees apart; under normal pressure they boil at 230.4°C and 242.6°C respectively (uncorrected). In this case, the azeotropic effect is so pronounced that separation by distillation does not require particularly efficient columns.

Indole is used commercially in several fields of chemistry. As might be expected from its occurrence in nature as a constituent of jasmine and orange blossom oils, it has long been used as a perfume fixative. The extraction of indole from coal tar in a state of purity which satisfies the perfume manufacturers is a chemical achievement since even trace amounts of impurity will falsify the aroma.

Indole is a starting material for growth-promoting substances and for amino acids. 3-Indoleacetic acid (indole-3-acetic acid) is one of the first growth-promoters

used. It is known commercially as heteroauxin. One way of making it is by the condensation of indole with formaldehyde and hydrochloric acid followed by condensation with potassium cyanide and hydrolysis of the resulting nitril. Alpha-amino-3-indole-propionic acid, known as tryptophane, is an integral component of many types of protein and one of the vital amino acids. 3-(Dimethylaminomethyl)-indole (gramine), obtained by a Mannich Reaction of indole with formaldehyde and dimethylamine, is an intermediate in the synthesis of tryptophane. Tryptophane is made by reacting gramine with acetaminomalonic ester and subsequent saponification.

Although the quantity of indole used is still small, improvement in the recovery process in recent years has resulted in steadily increased sales. Possibilities for indole are not at all exhausted with the uses mentioned. Interesting intermediates for dyestuffs and drugs can be made by reacting the hydrogen atom attached to the nitrogen. Of course, the relatively small amounts of indole in coal tar and the complicated methods for extracting and purifying it will never permit a price comparable to mass-volume products, but it is hoped that the recent advances in the preparation of indole will lead to a greater use of this interesting compound.

2-Phenylnaphthalene

Unlike indole, 2-phenylnaphthalene is a substance about which little can be said. Recently it was found that this compound, formerly classed among the rare constituents, actually is rather abundant in coal tar and can be recovered in relatively large amounts. The 2-phenylnaphthalene fraction boils below fluoranthene, so its recovery must be combined with that of fluoranthene and pyrene. Since there is no demand, 2-phenylnaphthalene is presently produced only in laboratory quantities. If a demand should develop the methylphenanthrenes, which boil below phenylnaphthalene, would become more accessible. There are considerable quantities of these in tar.

Isoquinoline/Quinaldine

As already mentioned, the only coal tar bases presently being used to any extent commercially are pyridine, pyridine homologues and quinoline. The problem of separating tar bases from their co-products is even greater than in the case of the neutral hydrocarbons. Crude bases are extracted from the appropriate distillation fraction by means of mineral acid from which they are subsequently liberated by the addition of caustic soda. Because of the complex nature of tar, distillation fractions do not contain only the particular tar base desired. Further, the formation of azeotropic mixtures between the hydrocarbons and the tar bases causes the latter to be distributed over a broad distillation range. Thus the extraction process invariably yields fractions which are mixtures of several compounds.

Isoquinoline and quinaldine are the most important compounds which occur with quinoline in the quinoline fraction. Since they boil above quinoline they occur in the distillation residue from which they could be recovered if a demand for them were to develop.

Table III

	<u>B.P. at Atmospheric Pressure - °C</u>
Quinoline	237.3
Isoquinoline	242.8
Quinaldine	246.9

There is extensive literature on the chemical reactions of isoquinoline and quinaldine. Isoquinoline is used as an auxiliary solvent in dyeing and as a starting product in the preparation of isoquinoline red and other cyanine dyestuffs, photographic sensitizers, drugs, pesticides, and vulcanization accelerators. Quinaldine can be used for similar purposes. The most important quinaldine dyestuffs include quinoline yellow, quinoline red, and ethyl red, as well as sensitizing dyes. Quinaldine can also be used as an inhibitor for metals and as a seed disinfectant. Although both these compounds could be produced in considerable volume, none of the uses has reached significant size.

Acridine Phenanthridine 7,8-Benzoquinoline

The three most important and most easily recovered tar bases in anthracene oil are acridine, phenanthridine, and 7,8-benzoquinoline.

Acridine is the best-known and occurs in the largest amount. None of the three bases has as yet been used on large scale, although interest in acridine has been increasing recently.

Acridine is in point of fact the base of numerous dyestuffs and drugs; but acridine dyestuffs are usually manufactured from 1,3-diaminobenzene and aliphatic or aromatic aldehydes. Even the syntheses of such well-known acridine derivatives as the drugs Trypaflavin (3,6-diamino-10-methylacridinium chloride) and Rivanol (2-ethoxy-6,9-diaminoacridine) do not usually involve acridine.

The extent to which 7,8-benzoquinoline occurs in coal tar has only been realized recently. Its only use at the present time is in the separation of meta and para cresol in gas chromatography. As with acridine, several drugs can be derived from phenanthridine; for example, quaternary salts of diaminophenanthridinium series have good trypanocidal properties.

Because of limited demand and the resulting high costs of producing very small batches of these compounds, the prices of acridine, phenanthridine, and 7,8-benzoquinoline are still high. Production on a larger scale--and the amounts of raw material are very adequate for this--would reduce costs considerably.

Thianaphthene Dibenzothiophene (Diphenylene Sulfide)

Thianaphthene and dibenzothiophene are the most abundant sulfur compounds found in coal tar. Thianaphthene is recovered with naphthalene, and the two can be separated only with difficulty because of their close boiling points (boiling points at one atmosphere: naphthalene 217.9°C; thianaphthene, 218.8°C). The formation of mixed crystals further complicates the separation.

The separation of phenanthrene and dibenzothiophene, the sulphur bearing compound that occurs with it, is not as difficult. The difference in boiling points is greater--(331.4°C; phenanthrene 336.5°C) and separation by distillation is more effective. Since dibenzothiophene distills just prior to phenanthrene, the limited market for phenanthrene has restricted the amount of dibenzothiophene recovered.

Both thianaphthene and dibenzothiophene could be recovered from coal tar in substantial amounts but it must be remembered that the cost would be high even if they were recovered on large scale.

Up to the present, very little use has been found for these two compounds. Thianaphthene has been used to some extent in the manufacture of drugs. Other proposed uses are the production of thioindigoid dyestuffs and herbicides from thianaphthene and preservatives with a fungicidal and bactericidal effect from dibenzothiophene. None has practical significance.

Besides the substances which have been discussed there are numerous other compounds that can be obtained from coal tar in relatively large quantities if needed. However, it should be remembered that the recovery and purification problem becomes more complicated as the concentration of the desired compound in the tar decreases. The economics of the processes are affected accordingly.

Attention is drawn to the dimethylnaphthalene fraction, which constitutes about 2 per cent of the tar and lies between the diphenyl and acenaphthene fractions. To date, the following nine dimethylnaphthalenes have been identified in coal tar:

1,2-dimethylnaphthalene	
1,3	"
1,4	"
1,5	"
1,6	"
1,7	"
2,3	"
2,6	"
2,7	"

1,6- and 2,6-Dimethylnaphthalene can be recovered relatively easily, but the isolation of the other compounds is very costly and complicated.

Anthracene oil has two interesting methylhomolog fractions: first, preceding the phenanthrene fraction is the methyl fluorene fraction which accounts for 1.8 per cent of the tar and includes 1-, 2-, 3-, 4-, and 9-methylfluorene; and secondly, following the carbazole fraction, the methylphenanthrene fraction which accounts for 1.8 per cent of the tar and consists mainly of 1-, 2-, 3-, and 9-methylphenanthrene as well as 4,5-methylenephenanthrene. The benzofluorene fraction, being the highest boiling portion of the anthracene oil, also deserves mention. Distilling after the fluoranthene fraction, it accounts for 1.6 per cent of the tar and consists mainly of 1,2-, 2,3-, and 3,4-benzofluorene, as well as 5,12-dihydrotetracene.

The coal tar pitch fractions offer a large reservoir of quadrinuclear and multinuclear aromatics. These need not be discussed because even though some pitch constituents can be recovered in large quantities, their separation is beset by difficulties which would preclude the possibility of cheap production even in volume. Reference has been made already to this problem under the discussion of chrysene.

Bulk tar constituents, with the exception of 1- and 2-methylnaphthalene, are all unsubstituted, binuclear and multinuclear aromatics which include only two heterocyclic compounds, dibenzofuran and carbazole. Special attention has been focused on fluoranthene which up to now has not received adequate attention, despite the fact that next to naphthalene and phenanthrene it is the most abundant constituent of coal tar:

This has been a review of coal tar products which could be made available in substantial quantities if a demand for them were created. The data show that very few aromatics, even those which are readily accessible, are presently used as pure products--or stating this thought in another way--there is a very large source of raw material available which has not yet been exploited.

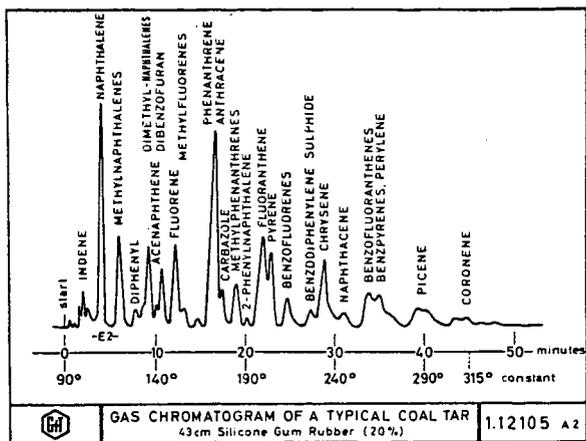


Fig. 1

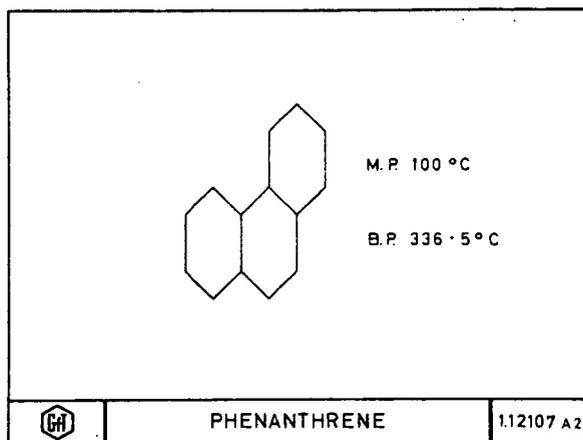


Fig. 2

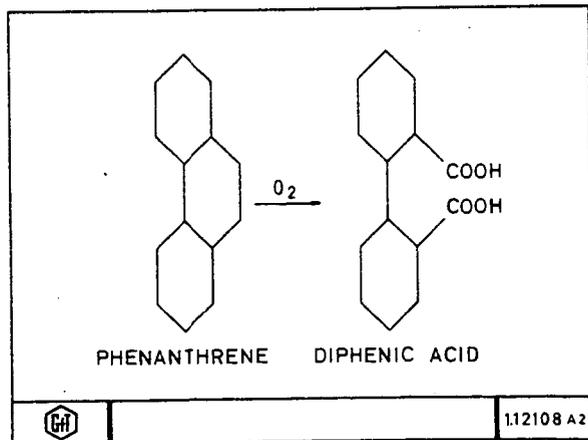


Fig. 3

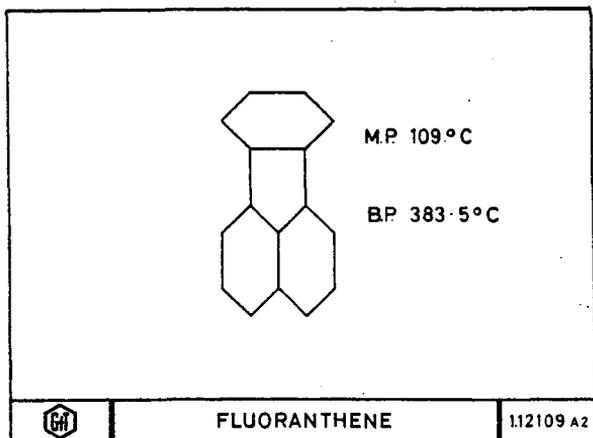


Fig. 4

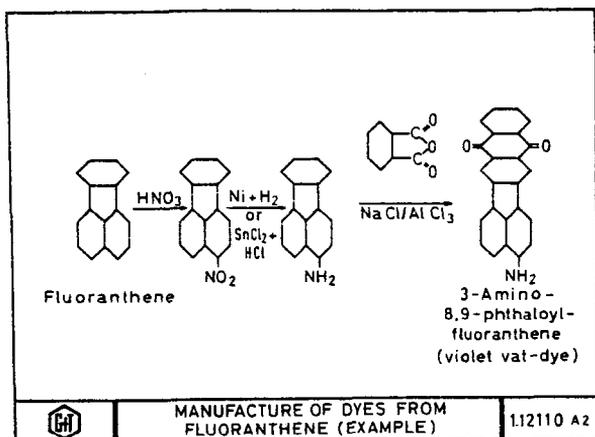


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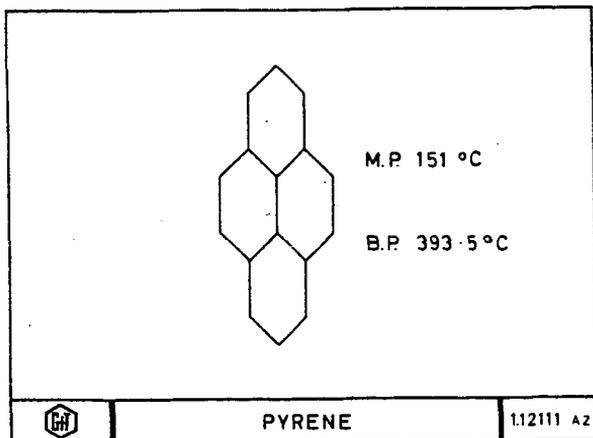


Fig. 6

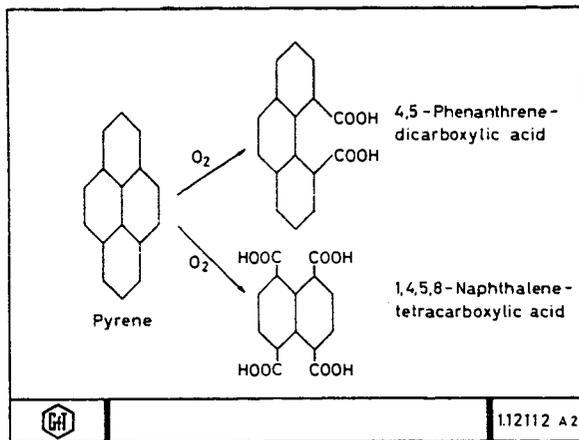


Fig. 7

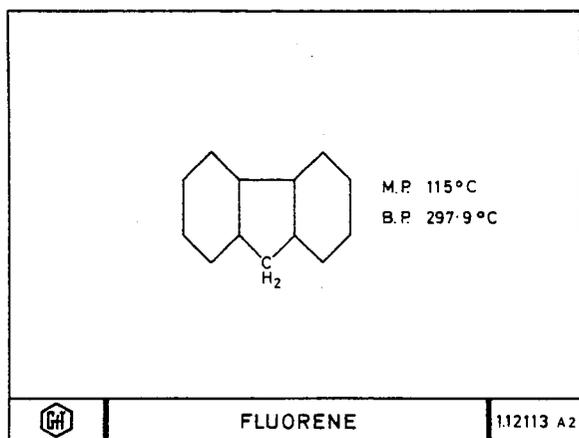


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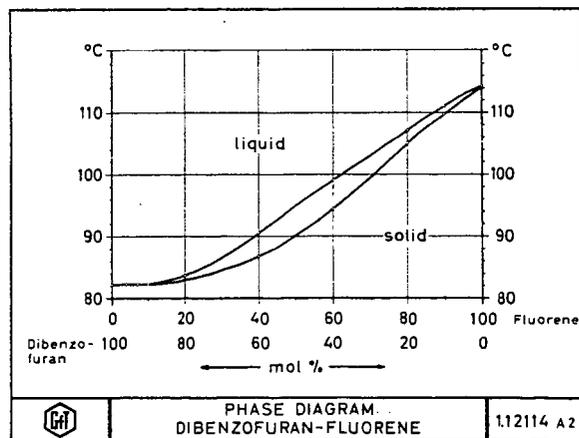


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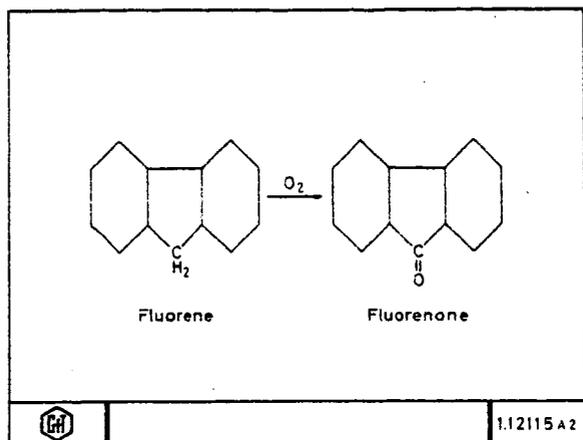


Fig. 10

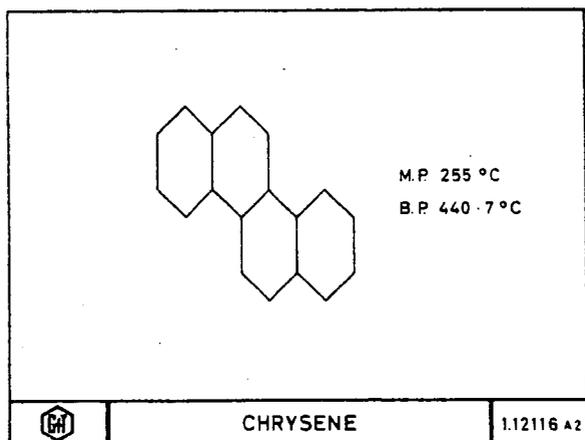


Fig. 11

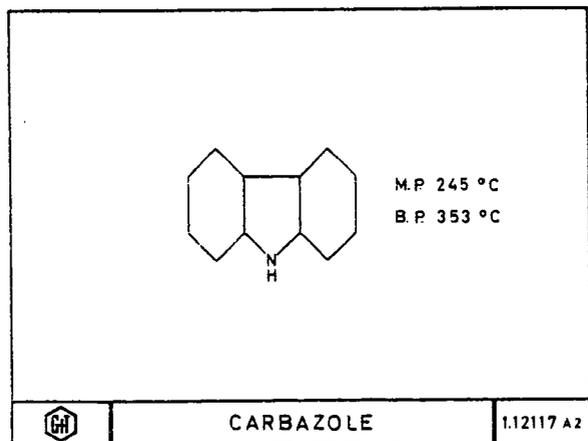


Fig. 12

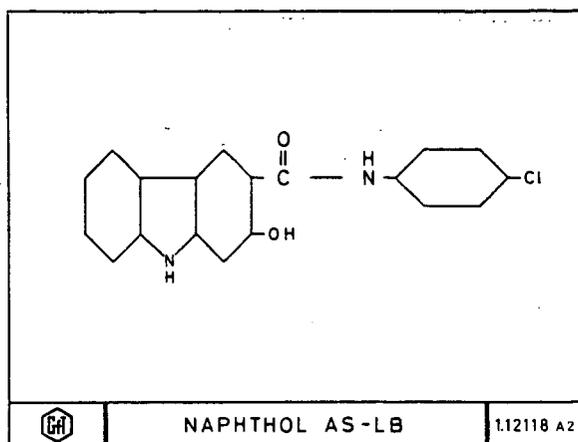


Fig. 13

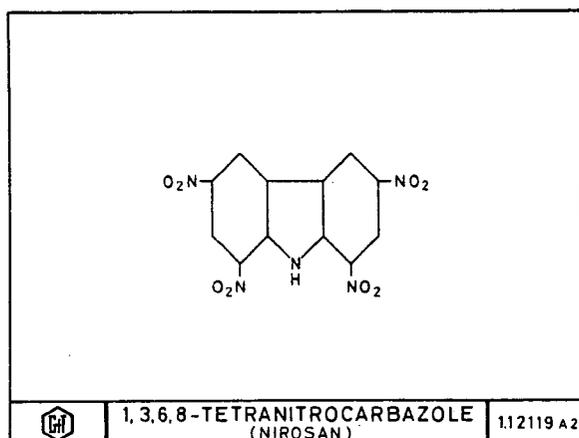


Fig. 14

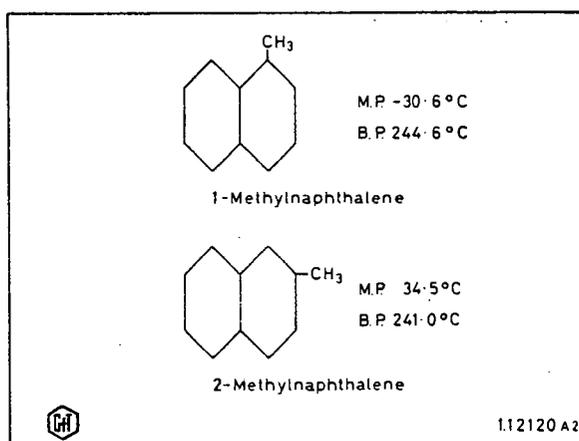


Fig. 15

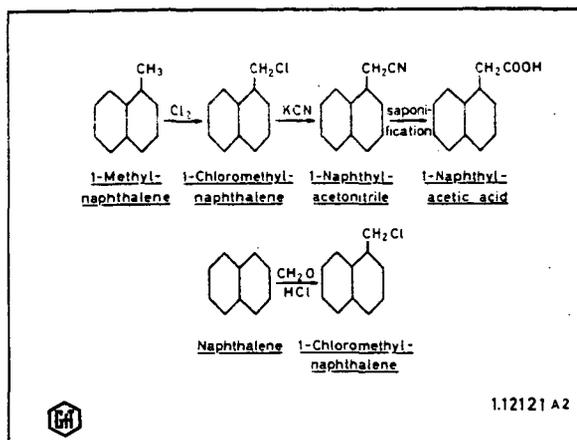


Fig. 16

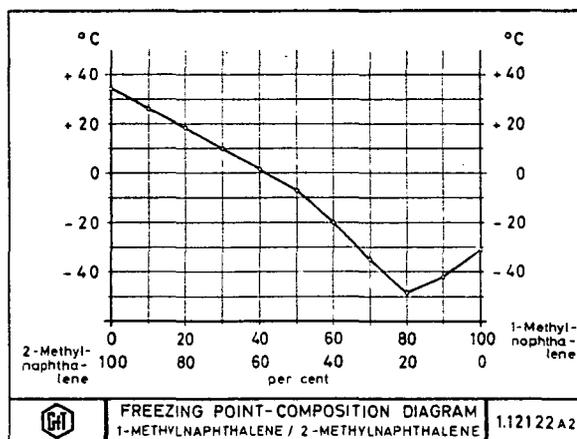


Fig. 17

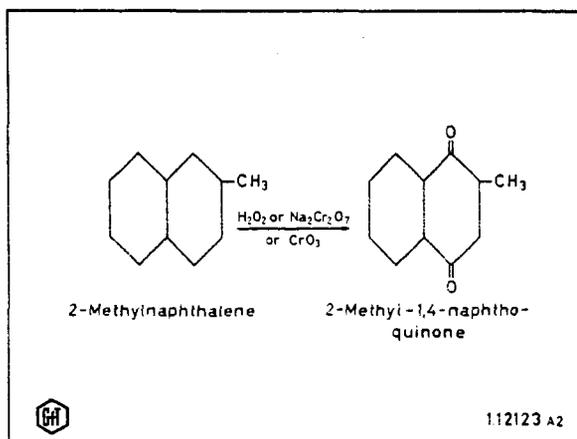


Fig. 18

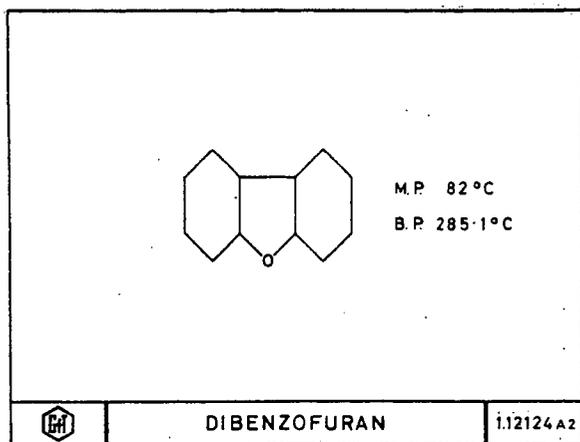


Fig. 19

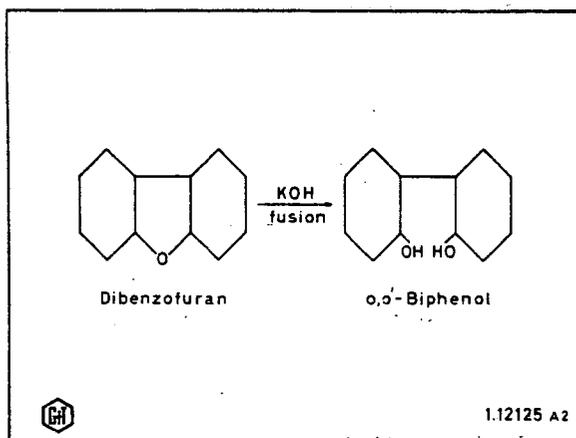


Fig. 20

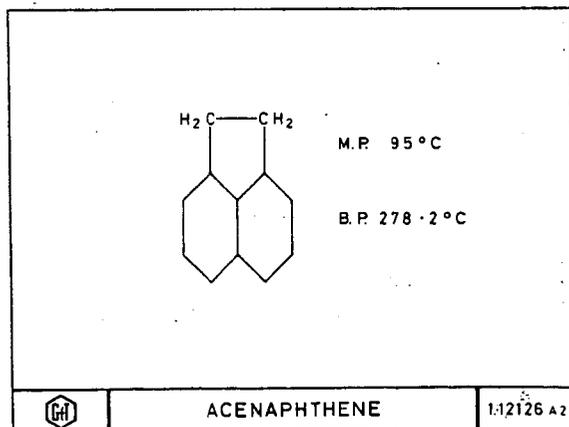


Fig. 21

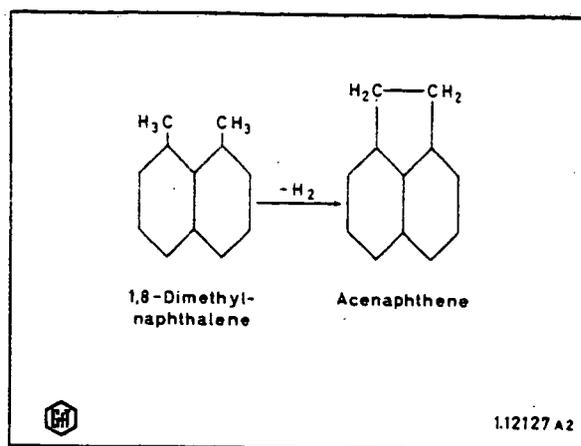


Fig. 22

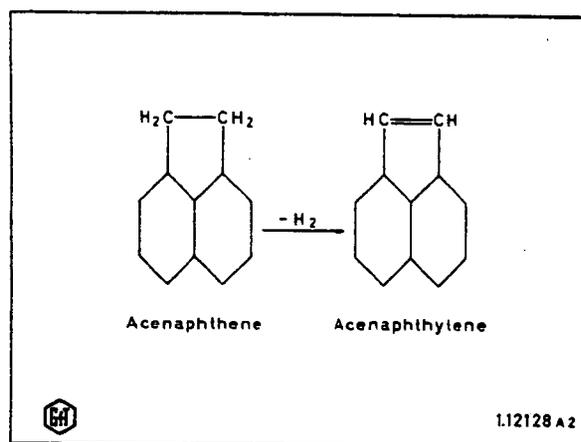


Fig. 23

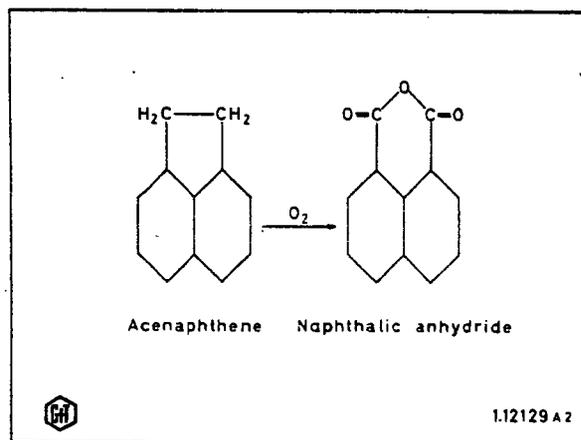


Fig. 24

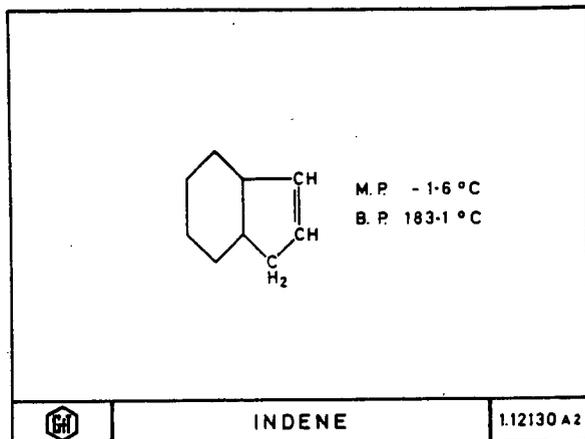


Fig. 25

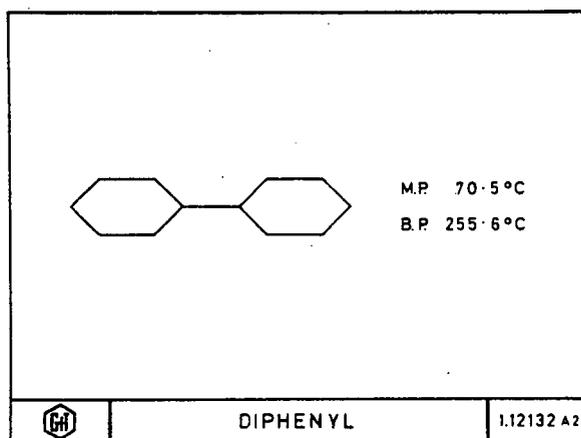


Fig. 26

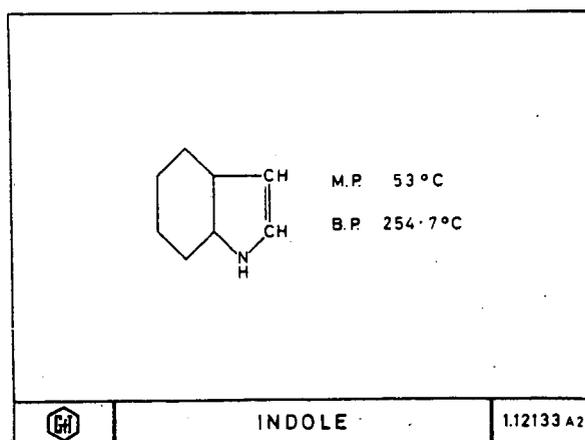


Fig. 27

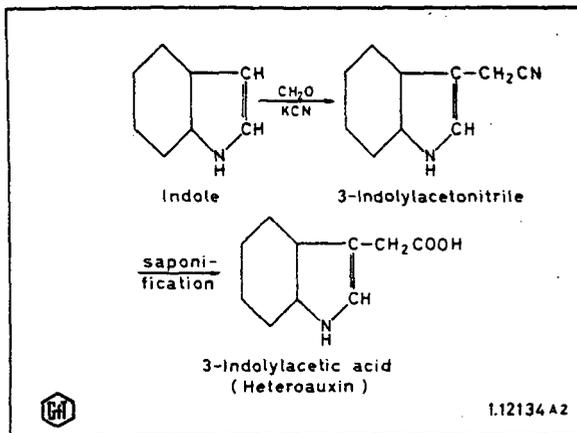


Fig. 28

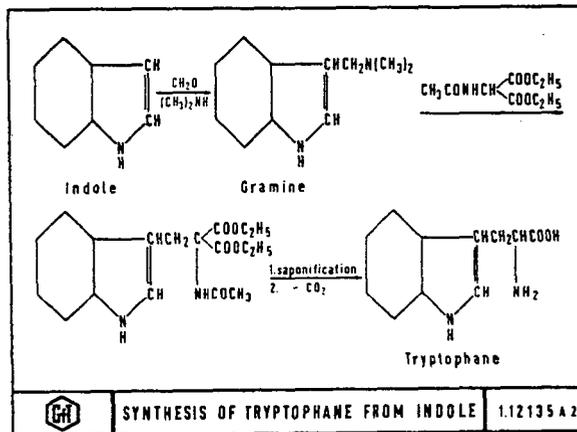


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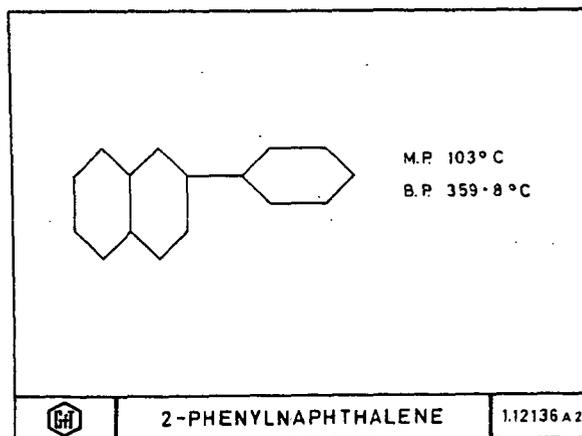


Fig. 30

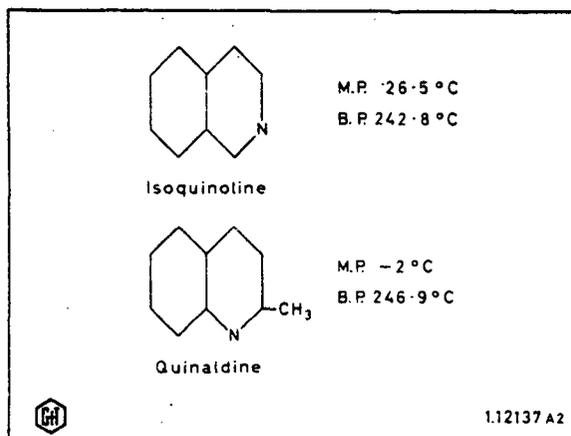


Fig. 31

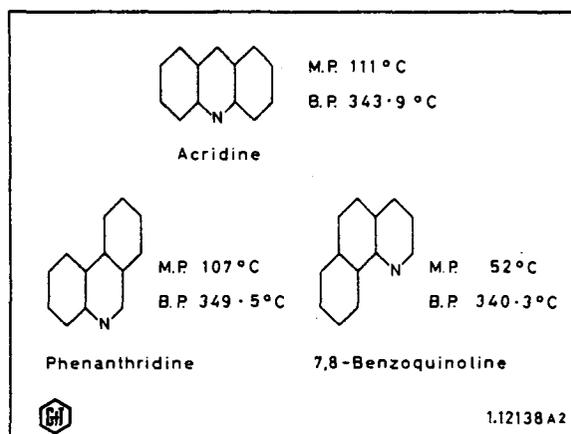


Fig. 32

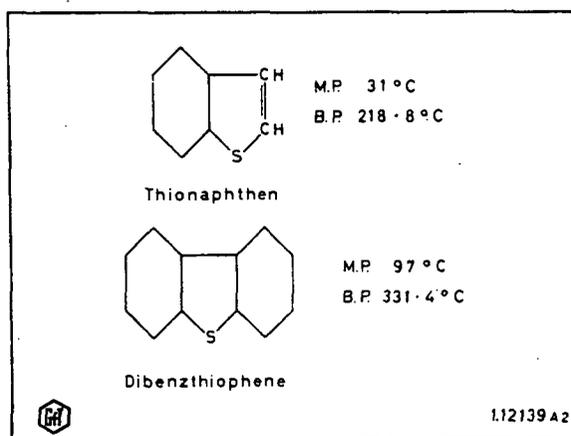


Fig. 33

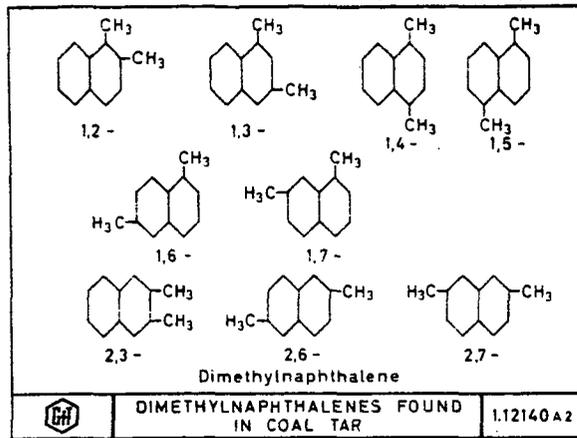


Fig. 34