KAWASAKI STEEL TECHNICAL REPORT

No.23 (October 1990)

R&D of High-Technology Research Laboratories,

Commemorating the 20th Anniversary

of the Technical Research Division

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The body can be viewed from the next page.

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1 Introduction

Recent technological progress has brought about an increased demand for high-performance and highly functional materials. Among these emerging materials are heat-resistive polymers for sophisticated electric and electronic parts, additives for human and animal foods, and varieties of intermediates for agricultural and pharmaceutical chemicals. These types of raw materials and products possess, in many cases, specific chemical structures in their molecules which are usually difficult to synthesize on a commercial basis.

Although coal tar consists of many components, mainly aromatic compounds, the number of single substances which are present in coal tar to a significant degree totals no more than thirty chemical species. The dominant compounds have been utilized in various fields; for example, light gas oils such as benzene, toluene and xylene and naphthalene are used for solvents and starting materials of various aromatic derivatives. Although coal tar contains significant amounts of many substances, these have not to date been fully utilized in the chemical industry. As the recent demand for functional materials grows, attention has been focused on unutilized specific aromatic compounds contained in coal tar. Technology for producing liquid crystalline polyesters, one of the heat-resistive polymers, from naphthalene derivatives as starting materials have been reported in the literature and many patents. In agricultural and pharmaceutical products, many intermediates and derivatives are produced from heterocyclic compounds such as indole and quinolines on a commercial basis. These types of heterocyclic compounds are contained in relatively large amounts in wash oil, which is obtained by the distillation of coal tar. Wash oil is a mixture of aromatic compounds having boiling points which range from about 200 °C to about 300 °C. **Table 1** shows an example of the typical composition of wash oil.

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* Originally published in *Kawasaki Steel Giho*, 21(1989)4, pp. 346-348

Table 1 An example of wash oil composition

Component	Content (%)
Naphthalene	10.3
Quinoline	5.2
β-methylnaphthalene	36.4
Isoquinoline	2.2
α-methylnaphthalene	14.8
Indole	3.9
Diphenyl	8.7
Dimethylnaphthalenes	3.9
Acenaphthene	4.7
Diphenylene oxide	3.1
Fluorene	1.9
Anthracene	2.1
Phenanthrene	2.1
Others	2.8

extended the production and sales of coal tar-related products such as light gas oil, naphthalene, phthalic anhydride and pitch. To stimulate further business expansion, the division promoted an R & D program to develop useful, new highly purified products which are separated from coal tar and refined. The target products are indole, quinoline, isoquinoline, quinaldine (2-methylquinoline), α-methylnaphthalene, β-methylnaphthalene, indene, indane, acenaphthene and so forth.

This paper describes a novel process and technology for producing tar-bases (quinoline, isoquinoline and others), indole and methylnaphthalenes from wash oil, the experimental results related to the process, and also a commercial plant at the Mizushima Works of Okayama, Japan. The processes and technologies employed, from basic research to the process and basic equipment design, were developed solely by Kawasaki Steel Corp.

2 Separation and Refinery Process for Tar-Bases and Indole from Wash Oil

2.1 Previous Technologies

Industrial recovery of tar-bases from wash oil was traditionally carried out by extraction using mineral acids, especially less expensive sulfuric acid[1]. The extracted tar-bases in an aqueous solution were then neutralized, recovered from the mixture by liquid-liquid separation and refined[2]. Further purification of tar-bases was carried out, in many cases, using a rectifying column equipped with a large number of theoretical plates[2].

Indole recovery from the tar-base-removed wash oil was carried out by one of the following three methods:

(1) Separation of indole from the tar-basc-removed wash oil by first forming a sodium hydroxide salt of indole, and then performing hydrolysis on the salt to obtain crude indole[3].
(2) Separation of indole by extractive distillation using a polar solvent[4].
(3) Extraction of indole using a polar solvent and distillation or crystallization of the extract[5].

The remaining neutral components were further isolated by distillation, if desired.

Since tar-bases and indole form azeotropes with neutral components contained in wash oil, highly purified tar-bases and indole cannot be obtained by distillation alone. Tar-bases and indole, however, could be concentrated, to some extent, by distillation. Accordingly, a combined industrial process for tar-bases and indole recovery was implemented, in which both secondary rectification and one of the above-mentioned methods were employed after obtaining the crude desired components which were concentrated preliminarily by a coal-tar distillation column[6].

2.2 A Novel Process for Tar Base and Indole Separation from Coal Tar

To develop a new process, the following basic policy was taken into account:

(1) The initial step was to separate the original wash oil into fractions of chemically similar components using a selective recovery method.
(2) Each desired component in the fraction was further isolated and refined based on the differences in the chemical or physical properties of the component.
(3) It was desirable to employ multi-purpose methods which could be applied to many kinds of products using the same equipment.

A schematic block diagram of the novel process is shown in **Fig. 1**. In the sulfuric acid treatment, basic components such as quinolines were extracted into the aqueous sulfuric acid layer, and the other components into the remaining wash oil in the oil layer. The aqueous sulfuric acid layer was washed with an organic

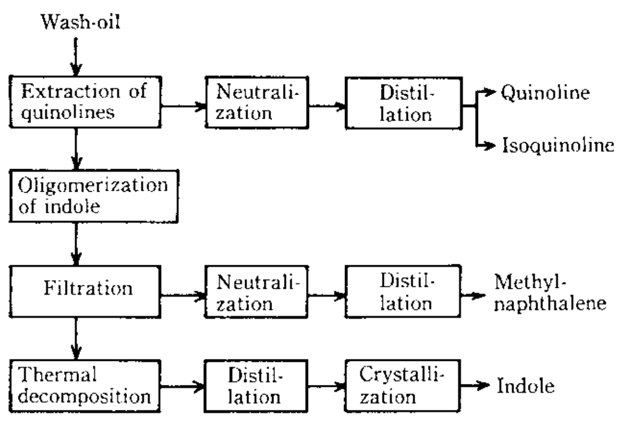

Fig. 1 Schematic flow of the wash oil separation process

solvent to remove oily residue components, and neutralized with alkali to form a water-soluble component layer and crude quinoline layer, which was rectified to isolate purified quinoline, isoquinoline and quinaldine with high yields. The oil layer, in which indole and neutral components such as methylnaphthalene are contained, was reacted with hydrochloric acid, producing solid indole oligomer, which was filtered out of the liquid-solid mixture. The remaining methylnaphthalene in the filtrate was purified by distillation to remove the small amount of remaining impurities. Indole oligomer, which still contained excess acid, was neutralized with alkali and converted to indole monomer by heat treatment. The indole monomer (crude indole) was further refined by azeotropic distillation and by crystallization using an organic solvent. The indole crystals were dried to remove the organic solvent adhered to the indole crystals, and the final product, indole, was obtained.

The features of the indole recovery process using the oligomerization method are as follows: indole in the starting material, such as wash oil in this process, can be almost totally recovered, even if the indole content is very low. Accordingly, refinery of methylnaphthalene by distillation in a downstream step can be easily achieved. In the indole monomer distillation step, in which crude indole is refined by the azeotropic distillation as described above, selection of the most preferable entrainer for the azeotropic distillation brings about a very high separation efficiency. In the purification steps, distillation columns which can be applied to a multi-purpose operation are employed. The features of this process lead to the economical merits which are essential for commercialization of the process.

In the following, experimental results for the operating conditions in the principal unit operations are described.

Although many nitrogen-involved components contained in wash oil show basic characteristics, indole is an exception, and shows weak acidity. The difference in the chemical properties between tar bases (quinolines) and indole provides the potential to separate them. However, in certain acidic conditions, indole formed oligomer due to protonation. In the extraction of tar-bases using sulfuric acid, it was essential to select suitable operating conditions in order to prevent the oligomerization of indole from occurring. **Figure 2** shows the relationship between the tar-base extraction ratio and the amount added of sulfuric acid. It was found that the amount of sulfuric acid required for the extraction was approximately equal to that of tar-bases under conditions of adequate liquid-liquid contact.

Operational difficulty in the liquid-liquid separation, after mixing the sulfuric acid, was affected mainly by the compositions of the wash oil, especially by the presence of low-content compounds. In the oligomerization step, the diameter of solid indole oligomer varied depending on treatment temperature, concentration of

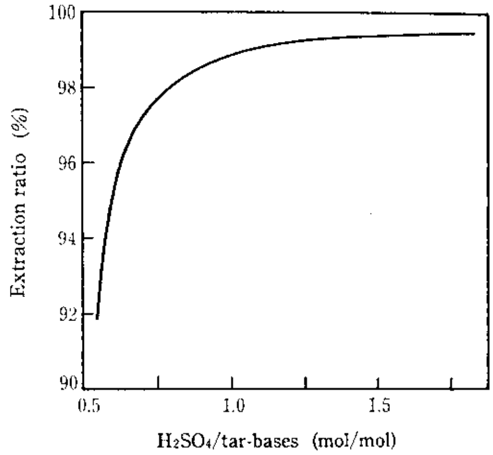

Fig. 2 Effect of sulfuric acid ratio on tar-bases removal

hydrochloric acid, hydrochloric acid feed method, and so forth. As the particle diameter became large, the filtration period in the next operation could be shortened, and the yield of indole oligomer could be enhanced due to the decrease in volume of mother liquor contained in the filter cake.

Indole oligomer was decomposed by heat treatment to produce indole monomer. After that, azeotropic distillation was carried out in order to efficiently remove neutral oil and impurities, specifically sulfur compounds, from the crude indole fraction, leaving relatively pure indole. A typical example of distillation curves using an entrainer is shown in **Fig. 3**, at which indole of around 90% can be obtained with a high yield.

For further purification of the indole, crystallization was employed as a finishing treatment. Crystallization using a suitable solvent was most effective to remove sulfur compounds of very low concentration. Recrystallization solvent consumption was closely related to the desulfurization percentage, which increased as the quan-

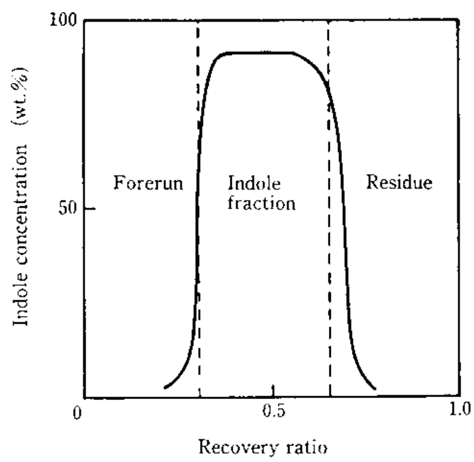

Fig. 3 Distillation curve

tity of recrystallization solvent used increased. As the diameter of solid indole crystals increased, the amount of mother liquor which adhered to the indole crystals decreased, and consequently the amount of impurities resulted from the mother liquor decreased as well. As a result, large crystals of indole provided a purer product. The same effect was obtained by washing the indole crystals with the fresh recrystallization solvent.

For the purification of crude quinoline and neutral oil fractions, distillation could be applied on the basis of the gas-liquid equilibrium. The distillation conditions could be easily estimated from the computer simulation.

With this process, the purity of the indole product was more than 98%. The purities of quinoline and isoquinoline were usually about 97% when a rectifying column with a large number of plates was used. The purities of α-methylnaphthalene, β-methylnaphthalene and the methylnaphthalene mixture were all more than 97% when the high-performance rectifying column was used. The precise purities of these products depend on distillation conditions.

A commercial plant based on the above-described process was constructed at the Mizushima Works. A recovery section corresponding to the upper half of the process flow diagram shown in Fig. 1 was put into service in November 1986, and a purification section corresponding to the lower half of the process flow diagram was completed in May 1988. **Photo 1** shows the indole production plant.

The plant has been smoothly and satisfactorily operated since the beginning of the operation. The operation of all the equipment has satisfied the design specifications.

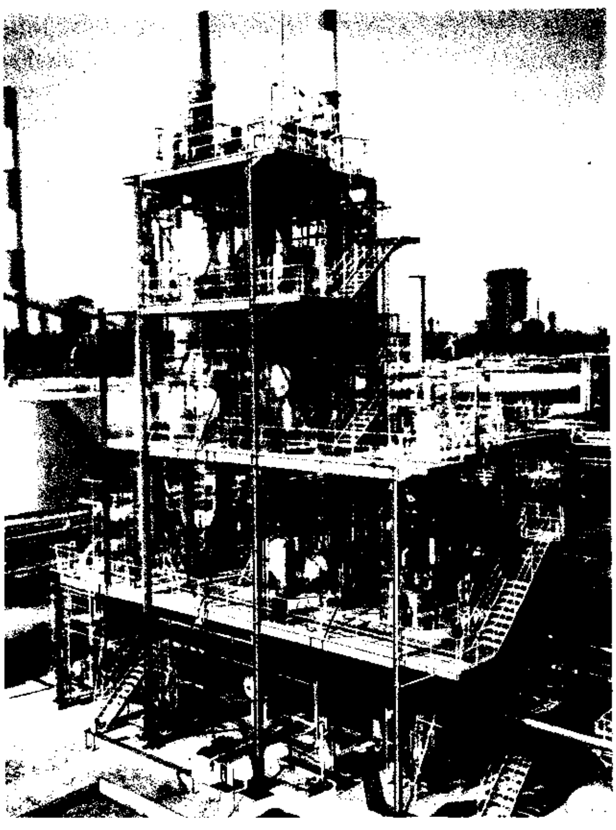

Photo 1 Indole refining plant at the Mizushima Works

3 Conclusions

The Chemical Division of Kawasaki Steel Corp. is promoting the production and sales of high-performance and functional chemical materials which are attained by the separation and recovery of useful chemical species contained in wash oil. For this purpose, a novel process has been successfully developed to separate quinolines, indole and methylnaphthalene from wash oil.

The features of this process are that the desired products are isolated and purified after preliminary separation based on the chemical property differences; that the oligomerization method is employed to separate indole from tar-base-removed wash oil; and that highly-purified β-methylnaphthalene can be produced. In addition, the multi-purpose equipment is employed in the separation and purification sections.

Construction of the plant, to produce tar-bases, indole, and methylnaphthalene, was completed at the Mizushima Works in May 1988, and the plant has been smoothly operated since the beginning of the operation.

During the basic research for the process development, useful comments were provided by Dr. Naoichi Sakoda of Sakoda's Chemical Research Laboratory (at that time), to whom the authors wish to express their sincere and deep gratitude.

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