Environmentally Compatible Hydrogenated Solvent

1. Introduction

When Nippon Steel Corporation manufactures coke, which is required for the steel making process, coal tar is produced as a by-product. Nippon Steel Chemical & Material Co., Ltd. gathers crude light oil, which is distilled from coal tar, and converts it into products of aromatic compounds (e.g., benzene, toluene, and xylene), etc., via desulfurization, fractional distillation, and other processes, adding value. These products are used as starting materials for various derivatives and also satisfy various needs for industrial solvents, etc. For those products, in recent years, there has been a move to introduce human safety and environmental compatibility as new viewpoints and this is more apparent in the industrial solvent sector. Thus, needs in the industrial solvent market have started changing. Although aromatic compounds (e.g., toluene and xylene) used to be regarded as omnipotent solvents, it was reported that they were harmful to health. In addition, follow-up surveys, etc., revealed that the cancer rate was high in people who had engaged in operations involving specific solvents, such as ethylbenzene and benzyl alcohol. Such solvents are now regulated by Japan's Industrial Safety and Health Act or voluntarily controlled by the industry; for example, use of such solvents is prohibited or people must wear safety gear, etc. when using such solvents. Also, chemical substance supervision organizations, represented by European REACH, in various overseas countries have started managing and regulating such solvents. In addition, other measures are being promoted, for example, management standards are provided to control concentrations of such solvents in waste water so as to prevent leaks into the environment from facilities, in addition to the protection of operators.

2. Efforts to Protect Environments

Under such circumstances, Nippon Steel Chemical & Material started, from early on, developing hydrogenated aromatic solvents to satisfy needs for less toxic solvents, in place of toluene and xylene.

In 1964, former Fuji Iron & Steel Co., Ltd. started operations to manufacture cyclohexane (nominal production: 33000 t/year) at the Hirohata Works. Cyclohexane is produced by hydrogenating benzene and is a raw material for caprolactam used to manufacture nylon fibers in Japan. The product supported the high economic growth in Japan along with steel, and increased the value of benzene.

Through this production of cyclohexane, Nippon Steel Chemical & Material had accumulated industrial-level hydrogenation process technologies for more than 30 years. As the next step, in 1998, the Hirohata Works of Nippon Steel Chemical Co., Ltd. at that time succeeded in commercializing methylcyclohexane, which was produced by hydrogenating toluene. The company started swing production (production using the same equipment by changing the raw material) between cyclohexane and methylcyclohexane to sell those products.

At the beginning, the company tried to sell methylcyclohexane by promoting "environmental compatibility," "hydrogenated solvent in place of toluene (aromatic compound)," and "low toxicity" as keywords. However, these keywords were not sufficient to motivate users to use methylcyclohexane in place of toluene, which they used at that time. We understand that users were reluctant to accept the cost increase to add a hydrogenation process with toluene as a raw material, in particular. However, the paint, ink, and adhesive industries that used a large amount of toluene and xylene started gradually understanding that operators must be protected from the risk of toluene and xylene and that environmental compatibility was required from a social perspective. Lately, the demand for methylcyclohexane in Japan has been confirmed to be more than 10000 t/year and the demand is further increasing these days.

Cyclohexane and methylcyclohexane manufactured by Nippon Steel Chemical & Material are highly valued for their high purity. Although this is partly because the raw materials (benzene and toluene) are highly pure, management in manufacturing processes is also important. Attention is particularly required to manage the quality of catalysts. Nippon Steel Chemical & Material uses Ni/diatomite as catalysts. However, a deposit of diatomite may run out and mining of another deposit may be started. In such a case, impurities (a minute amount of secondary products) in products may increase or the distribution may change. Accordingly, it is necessary to retain the high purity of products by evaluating candidates of succeeding catalysts that catalyst suppliers submit in advance and adopting catalysts having the same performance as the conventional catalysts.

3. Toward the Multiproduct

In addition to methylcyclohexane, the company had been working to reduce the toxicity of aromatic solvents through hydrogenation and develop proprietary products through hydrogenation. In 2002, a batch-type hydrogenation plant, which was able to hydrogenate materials even in a small amount, was established at the Hirohata Works of Nippon Steel Chemical at that time and it started commercial operations. This plant is used to hydrogenate ethylbenzene and naphthalene and prototype new hydrogenated products under development as well as to perform a hydrogenation process under contract.

Table 1 lists the current product lineup. The major characteristic of hydrogenated solvents of Nippon Steel Chemical & Material is

Table 1 Product list

Product name	Abbreviation	Purity*	Source
Cyclohexane	PCH	99.9%	Benzene
Methylcyclohexane	MCH	99.9%	Toluene
Ethylcyclohexane	ECH	99.99%	Ethylbenzene
Decahydronaphthalene	DHNA	99.99%	Naphthalene
Tetrahydronaphthalene	THNA	99.84%	Naphthalene

*Actual result

Table 2 Properties

		Environmentally compatible products					Aromatic	
		PCH	MCH	ECH	DHNA	THNA	Toluene	Xylene
Formula CAS		C_6H_{12} 110-82-7	C_7H_{14} 108-87-2	C_8H_{16} 1678-91-7	$C_{10}H_{18}$ 91-17-8	$C_{10}H_{12}$ 119-64-2	C_7H_8 108-88-3	C_8H_{10} 1330-20-7
Properties	Boiling point (°C)	81	101	131.8	186	207	110.6	136–139
	Specific gravity (15°C/4°C)	0.78	0.77	0.78	0.88	0.97	0.87	0.87
	Flash point (°C)	−18	−4.3	19	56	72	5	24
	Viscosity (mPa・s)	0.98 (20°C)	0.73 (20°C)	0.78 (25°C)	2.85 (20°C)	2.41 (20°C)	0.59 (20°C)	0.58 (25°C)
	Surface tension (mN/m)	25.3 (20°C)	23.8 (20°C)	23.1 (20°C)	29.7 (20°C)	34.7 (20°C)	28.5 (20°C)	28.6 (20°C)
	Water solubility	58 ppm (25°C)	14 ppm (25°C)	6.3 ppm (20°C)	0.9 ppm (25°C)	45 ppm (25°C)	450 ppm (25°C)	200 ppm (20°C)
Solubility	Solubility parameter	8.1	7.9	8.0	8.5	9.7	8.8	8.8
	Aniline point (°C)	30.2	40.3	43.8	33.6	below 5.0	below −30	below −30
Regulatory	Fire Service Act category 4	First-class petroleum	First-class petroleum	First-class petroleum	Second-class petroleum	Third-class petroleum	First-class petroleum	Second-class petroleum
	Poisonous Material Control Law	n/a	n/a	n/a	n/a	n/a	Deleterious substance	Deleterious substance
	Pollutant Release and Transfer Register (PRTR)	First-class	n/a	First-class	Second-class	n/a	First-class	First-class
	TLV (ppm)	150	400	n/a	n/a	n/a	50	50

Table 3 Usage example

PCH	MCH	ECH	DHNA	THNA
Rubber Forming agent Optical film Intermediate of medicine	Ink, Paint Adhesion bond Cleaning agent Intermediate of medicine	Ink, Paint Cleaning agent Dyeing agent Intermediate of medicine	Ink, Paint Cleaning agent Engineering plastics	Ink, Paint Cleaning agent Intermediate of medicine

their high purity. In addition to the fact that the solvents contain almost no impurities, the hydrogenated solvents can reduce loads in processes for controlling the volatility in a narrow boiling point range and collecting, distilling, and regenerating solvents after use, compared to the case where mixed solvents are used for which the boiling point ranges are large.

Table 2 lists the detailed properties of the products and **Table 3** lists the typical usage examples. For these hydrogenated solvents, although the toxicity (e.g., carcinogenicity) has been reduced by turning aromatic compounds (benzene rings) into alicyclic compounds (cyclo rings), the solvency has also decreased at the same time. Accordingly, in many cases, customers and special manufacturers (e.g., thinner manufacturers) compound new solvents depending on the solute to use them while, in some cases, toluene can be simply replaced with methylcyclohexane. Because proprietary expertise and development capability are required to compound new solvents, customers themselves can promote the added value to the market.

In addition, the management and disuse of aromatic solvents and other substances that adversely affect human bodies and environments are a world trend. Rather than users who actually use such substances in their manufacturing processes, end distributors, which ultimately sell products to consumers, are actively appealing to consumers; for example, they demand that substances for which there is concern regarding harmful influence be prohibited or demand product development roadmaps on the assumption that such substances will be prohibited in the future.

As indicated above, the demand for hydrogenated solvents is expected to increase in the future as well and Nippon Steel Chemical & Material is determined to satisfy such demand through perfect arrangements. In addition, regarding a hydrogenation process that we perform under contract, we give consideration using multiple 0.2 to 20-L reactor vessels and then prototype and mass-produce solvents in cooperation with the research and development department.

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