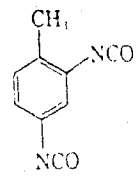
EXECUTIVE SUMMARY

The technology status study report on isocyanates namely toluene diisocyanate (TDI) and diphenyl methane diisocyanate also called methylene bis phenyl diisocyanate (MDI), is prepared covering the production technologies, end uses, state of art, international scene, status of Indian industry technological gaps etc. This report enables to assess the state of art of Indian industry, identification of technological gaps and measures to be taken to fill the gaps including the need for import of technology if needed.

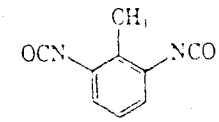
The production of TDI and MDI has grown at a rapid rate in past thirty years (~6% annum) and world production capacity now stands at over 2.5 million tonne per annum after the discovery of polyurethanes in 1937.

I. TOLUENE DIISOCYANATE (TDI)

TDI is a Colourless liquid and generally used as a 80 : 20 blend of 2, 4 and 2, 6 isomers.



2,4 isomer

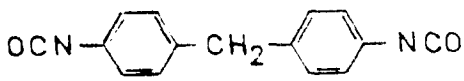


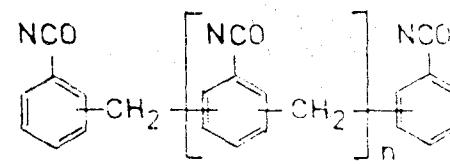
2,6 isomer

However, 65 : 35 blend of 2, 4 and 2, 6 isomer is also reported to be in use in Europe.

II. DIPHENYL METHANE DIISOCYANATE OR 4.4'-METHYLENE BIS (PHENYL ISOCYANATE) (MDI)

It is the most important isocyanate for polyurethane applications. The 4, 4'-isomer (pure MDI) is a colourless solid of low melting point (37—38°C).





4, 4'—Diphenylmethane diisocyanate Polymethylene Polyphenylisocyanate (PMD). The principal commercial product is an undistilled mixture known as polymeric MDI

(PMDI) containing 40%-60% mixture of 4, 4'-isomer together with other isomers of MDI.

III. END-USES OF TDI AND MDI

Major applications of these isocyanates are in manufacture of flexible and rigid foams, spandex fibres, coatings, elastomers, adhesives, microcellular sponages, synthetic leather etc. The non-polymeric applications of these isocyanates lie largely in the field of insecticides, herbicides and other biologically active compounds.

For more than 35 years, TDI has been used for manufacturing flexible polyurethane foams with a great success, to a point where its foam is considered as the outstanding product for cushioning.

MDI is used mostly for rigid polyurethane foam manufacture, which are highly cross-linked cellular polymers with a closed cell structure; each bubble within the material has unbroken walls in order to restrict gas movement and thus have excellent thermal insulation.

In the case of polyurethane elastomers, MDI is used largely for the thermoplastic and millable type, while TDI for the thermosetting type.

IV. MANUFACTURE OF TDI AND MDI

Commercially TDI is manufactured by well known conventional route involving phosgenation of toluene diamine. Initially the nitration of toluene is carried out using the mixture of nitric and sulphuric acids to give dinitro toluene, which is reduced to toluene diamine usually in the presence of nickel or palladium catalyst. Almost all commercial manufacturing process for TDI in use to date are based on continuous liquid phosgenation method, in which the toluene diamine mixed isomers or its hydrochlorides in an inert solvent such as O-dichlorobenzens or xylene are reacted continuously together with excess liquid phosgene. After phosgenation, the climbing-film and thin-film evaporators, are used to separate TDI from the non-volatile but reactive by-products without delay. Further purification is done by using conventional fractionating columns or crystallization. Non-phosgenation route for TDI has been developed but not fully commercialized.

The commercialized conventional phosgene process for MDI, consists of three reaction steps i.e., condensation of aniline with formaldehyde in the presence of hydrochloric acid, neutralisation of the hydrogen chloride salts of methylene dianiline and the higher polyamines, and phosgenation of the amines coinciding with decomposition of the amines coinciding with decomposition of the carbamoyl chlorides as intermediates. Pure MDI is obtained by distillation or crystallization of polymeric MDI.

Pure MDI obtained from conventional phosgenation process, is having disadvantage of being solid at room temperature, in some applications like RIM processing. Technology for the liquid MDI have been developed by shell chemical using modified phosgenation process.

BASF has developed a high pressure-temperature process for the production of MDI, which is not having disadvantage of conventional phosgenation process like slow rate of reaction and liberation of highly toxic phosgene during heating the reaction mixture to the final phosgenation.

Manufacture of MDI is also being done at pilot-plant scale by non-phosgenation route involving catalytic oxidative carbonylation of aniline to ethyl phenyl carbamate (EPC), catalytic condensation of EPC with formaldehyde to methylene diphenyl diurethane (MDU) and decomposition of MDU to form MDI. But non-phosgenation route is not fully commercialized.

V. HEALTH AND SAFETY ASPECTS

Isocyanates are classified as dangerous substances (EEC guidelines). They are usually labelled "toxic" and should be handled with care. Exposure to atmospheric moisture must be avoided. Isocyanates cause irritation when applied directly to the skin of the rabbits or to their eyes. Reported inhalation causes tracheobronchitis, bronchitis, emphysema and bronchopneumonia, according to exposure concentration and frequency. Some sensitization and asthma like reactions can occur upon exposure to TDI or MDI. Exposure limits have been set by OSHA at 0.02 ppm, for an a hr IWA.

VI. NATIONAL SCENE

The isocyanates are not produced indigenously but have been imported and used by a large number of processors for different uses like polyurethane foams, both rigid and flexible, PU shoe soles, PU adhesives, inks, varnishes, paints etc. The technology for these isocyanates production is to be imported as no proven indigenous technology is available.

The project of setting up a plant for production of TDI and MDI got a jolt due to the Bhopal gas tragedy. However, Hindustan Organic Chemicals (HOC), a Public Sector Undertaking has been issued licence to set up a plant for production of TDI in collaboration with AB Chematur of Sweden who are the licensors for DU Pont's technology while search is reported to be on for the technology source for MDI. It is also reported that besides, TDI and MDI manufacture, HOC is reported to have plans for setting up of 10,000 TPA polyurethane systems at an estimated cost of Rs. 15 Crores. Now ICI India is also having LOI for MDI while Manali Petrochemicals is having for both TDI and MDI.

VII. DEMAND AND GROWTH (NATIONAL)

In India TDI and MDI are consumed alongwith polyols in polyurethane (PU) foam manufacturers while the TDI is used to manufacture flexible PU foams, MDI is mainly used to manufacture rigid foams. The total demand of TDI and MDI put together is approximately 12,000 TPA, and totally met by imports. Unlike in the West, where rigid PUs have larger share of market, flexible PUs have better market in India. In India mattress manufacturers are the major consumers of these isocyanates.

Recently, Urethane India Ltd., a subsidiary of Chemicals and Plastics India Ltd., have started producing thermoplastic polyurethane resins (TPUs) using 99.9% pure MDI, in collaboration with M/s. B.F. Goodrich Chemical Company of USA and are planning to increase the production by ten folds by the end of this century. The rigid PU foam is also used in India for refrigerator insulation; interior panelling, wing tips, insulation, radar covers etc. of air crafts; car bumpers, instrument panels, stearing wheels, roof insulation of automobiles; and finally for a number of strategic applications for naval equipment.

Apart from the above areas of applications, shoe manufacturers are the other consumers of PU foams. It is learnt from the local consumers of these isocyanates and polyurethanes that there is considerable growth for these isocyanates.

VIII. INTERNATIONAL SCENE

A major part of world's isocyanate production is shared by the two isocyanates namely TDI and MDI. The production capacity now stands over 2.5 million tonne and a growth rate of 3% per annum is forecast, although prices of TDI and MDI have fallen in 1991 due to overproduction of these isocyanates and less growth in consumption. This less growth in consumption was attributed to the proposed restriction and ban on CPCs and political instability in Eastern Europe. The hazards associated with these including the raw material phosgene have restricted their production to large chemical companies like Du Pont, ICI, BASF, Mitsui etc. who are well equipped with sufficient security and safety provisions to handle any mishaps.

IX. RESEARCH AND DEVELOPMENT

The National R & D indicates that no research is going on for development of technologies for production of TDI and MDI either by phosgene or non-phosgene route. However, Shriram Institute for Industrial Research did carry out a preliminary work on development of technology of TDI but had to abandon after the Bhopal gas tragedy. It is learnt that a lot of work is going-on on urethanes and other applications of TDI and MDI in the other institutes. Vikram Sarabhai Space Centre have developed a series of propellants for sounding rockets and launch vehicles, compatible inhibitors and liners for rocketry, flexible and rigid PU foams for cryo-insulation etc. Work is still going on at VSSC on high energy propellants, micro cellular elastomers etc. Indian Institute of Chemical Technology, Hyderabad, have developed and commercialised

single and double pack PU binders, enamels and PU based rigid and flexible foams. Now IICT is working on CFC substitutes for rigid foams.

Indian Institute of Technology, Delhi have used these isocyanates for the development of urethane acrylate resins.

Besides the above research institutes, Central Drug Research Institute (CDRI) was involved in studying the toxic effects of these isocyanates.

X. SPECIFICATIONS

There are no Indian Standards/Specifications available for testing of TDI and MDI. However, there are specifications available for PU foams.

XI. LATEST TECHNOLOGY AND DEVELOPMENTS

On the international scene efforts are on to manufacture TDI and MDI by the non-phosgenation route. Also some of the giant companies like M/s Mitsui of Japan,' M/s Asahi (Japan), M/s Shell Oil Company of USA have even obtained patents for production of these isocyanates by non-phosgenation routes. But this process is carried out only on pilot plant scale and no commercial plant is reported to have come up so far.

After the slump in growth rate of 1980's (7-8%) in 1991, it is quite evident that the growth potential of TDI and MDI hinges on resolving the issue of CFCs in flexible and rigid foam, which make-up 2/3 of the polyurethane market.

For flexible foam the technology is already in place to move from CFC blowing agents to water blown formulations. But problem exists in the case of rigid polyurethane foams due to requirement of comparative thermal insulation properties, toxicity test and commercial production of CFC substitutes like HFC 134a, HCFC 141b, LBL2 etc., which wants development.

XII. TECHNOLOGY ABSORPTION AND GAPS

On the technological front of production of TDI and MDI, no gap could be identified as there is no indigenous production. However, on the processors front, Urethane India have imported technology from B.F. Goodrich of USA for making thermoplastic PU elastomers from pure MDI. Major technology gap has been identified in the case of flexible foam manufacture which are generally using hand-mixing methods allowing more losses in yield and hazardous with pollution control in view. Besides this, in the case of thermoplastic polyurethane elastomers, there is only one manufacturer in the country and many important grades like, high flexibility are not available. Also technology needs development for the block polyurethanes in the country.

XIII. RECOMMENDATIONS

1. Aslthough Hindustan Organic Chemicals, Manali Petrochemicals, ICI India, etc. intend to go for production of TDI and MDI and are making efforts but, further progress is almost nil. Efforts have to be intensified by LOI holders for the indigenous production of these isocyanates.

2. Due to highly toxic nature of these isocyanates, all the safety measures must be given utmost priority by proposed TDI and MDI manufacturers in the production plants of these isocyanates and phosgene.

3. The present consumption of TDI and MDI is about 12,000 tonne in India. If all the TDI and MDI plants, for which LOIs have been issued, come on stream, then other growth areas for indigenous applications and export potential of these isocyanates have to be identified. Initiatives may be taken by various LOI holders and research organisations for development of probable growth areas and export potential.

4. Research and development programmes may be taken by various research organisations on non-phosgenation routes of production of TDI and MDI which can obviate the utilization of highly toxic phosgene, the main hindrance in the production of these isocyanates in the country.

5. Some end users of these isocyanates are having old technologies and crude methods, which are having losses in yield and are not safe with pollution control in view. These may be updated keeping in view the high cost and toxic nature of the substance.

6. Suitable technology have to be developed for the production of block Polyurethanes which are having significant commercial importance.