A Survey on Diisocyanates and Polyol Manufacture for Polyurethane Production in Nigeria

Reginald Umunakwe[1], Chioma Ifeyinwa Madueke[2], Kelechi Chukwunyere Uchehara[3]

[1]Department of Materials and Metallurgical Engineering, Federal University Oye-Ekiti, Ekiti State,
[2]Technical Services Manager, Nagode Industries Limited, Ikeja, Lagos, NIGERIA.

[1]reginald.umunakwe@fuoye.edu.ng, [2]chioma.madueke@fuoye.edu.ng

ABSTRACT

This technical paper reviews the production of the major chemicals for polyurethane production in Nigeria. The market for polyurethane products like foams and mattresses in Nigeria is so large that a host of companies are engaged in the production and sales of such products in the country. It is however regretted that the major chemicals, diisocyantes and polyol required for polyurethane production are totally imported into Nigeria despite the abundance of petroleum which is the major source of the raw materials. This review calls for a feasibility study on the establishment of the plants for the production of diisocyanates and polyol in Nigeria.

Keywords: Diisocyante, Polyol, Polyurethane

INTRODUCTION

The production of polyurethane involves the reaction between diisocyanate, polyol and other chemicals. Polyurethane types range from flexible foams to tough, stiff elastomers and are used in diverse consumer and industrial applications.

Diisocyanate + Polyol $\longrightarrow$ Polyurethane polymer + Heat

Polyurethane is not sold as ready-made polymers but as precursors usually polyols and diisocyanates that are mixed at the conversion stage (Boustead, 2005). Polyols contain the -OH group while diisocyanates are compounds containing the –NCO groups. The primary reaction is of the form;

-NCO + OH $\longrightarrow$ -NH-CO-O-

diisocyanate + polyol $\longrightarrow$ polyurethane polymer + heat

The diverse applications of polyurethane include mattresses, furniture, automobile seating, carpet underlay bedding, noise attenuation, building insulation, refrigerators and for cups of hot drinks (Rankow, *et.al,* 1971; Nexant, 2008). The production of polyurethane based on different applications is shown in *figure 1*while the production based on the type of polyurethane is shown in *figure 2* (Allport**,** *et.al.,* 2003). Flexible polyurethane foam is a versatile material, environmentally neutral and sustainable values to the products and manufacturing processes in the flexible polyurethane foam (FPF) have been brought (Polyurethane Foam Association, 1991; Polyurethane Foam Association, 2011). The latest Ceresana's studies show that the global polyurethane demand will continue to rise by 4.5% per annum with Asia –Pacific currently the prime market for polyurethane with about 44% demand followed by North America and Western Europe (Ceresana Market study, 2013).The

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regional production of polyurethane in 1998 is shown in *figure 3* with Asia pacific specified as the region with high growth (Allport**,** *et.al.,* 2003).

RAW MATERIALS FOR POLYURETHANE PRODUCTION

The major raw materials for the production of polyurethane which are diisocyanates and polyols are made from crude oil and natural gas. The properties of the commercial products are controlled with a number of ancillary chemicals and processing aids which are also required. The other chemical required include catalysts, surfactants, chain extenders or cross-linkers, fire retardants, fillers, pigments and blowing agents. *Table 1* gives the typical components of polyurethane formulation (Allport**,** *et.al.,* 2003).

Diisocyanates

Diisocyanates which have the greatest commercial value are produced from aromatic compounds benzene and toluene (Boustead, 2005; Nexant, 2008). Diisocyanates of greatest technical importance are toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI). Toluene diisocyanates are used for flexible polyurethane foams while diphenylmethane diisocyanate are used for rigid, flexible or elastomeric polyurethane foams. *Figure 4* shows global demand of toluene diisocyanate by end use (Nexant, 2008). Diphenylmethane diisocyanate and toluene diisocyanate are produced in large tonnage and comprise about 90% of the total diisocyanate market (Allport**,** *et.al.,* 2003). 85% of the global toluene diisocyanate is demanded for polyurethane production and this drives the toluene diisocyanate market (Nexant, 2008). The potential respiratory health hazard associated with toluene diisocyanate is reacted out during the manufacture of flexible polyurethane foam and in the end does not present any risk to end users and environment (Polyurethane Foam Association, 2011**)**.

Production Of Toluene Diisocyanate

A three-step process is employed in the production of toluene diisocyanate; viz, nitration of toluene to dinitrotoluene (DNT), reduction of dinitrotoluene to toluene diamine (TDA) and phosgenation of TDA to toluene diisocyanate. These processes for toluene diisocyanate operations are combined in an integrated plant sites which does the major production of toluene diisocyanate. The economies of three toluene diisocyanate plant processes have been compared and evaluated (Nexant, 2008). Commercial toluene diisocyanate are usually a mixture of the 2,4- and 2,6-isomers usually at a ratio of 80:20. Figure 5 shows the structures of the isomers.

Production Of Diphenylmethane Diisocyanate

The production of diphenylmethane diisocyanate basically starts with the nitration of benzene by mixed acid (nitric acid and concentrated sulphuric acid) and followed by the production of aniline by the catalytic hydrogenation of nitrobenzene. Diphenylmethane diisocyanate is then produced as monomers and polymers by the acid-catalyzed, liquid phase condensation of analine and formaldehyde which is followed by the liquid phase phosgenation of diphenylmethane diamine (MDA) to diphenylmethane diisocyanate. Not less than 80% of analine produced is used in the production of diphenylmethane diisocyanate (Linch and Linda, 2012). The process chemistry for the production of diphenylmethane diisocyanate has been reported as well as the global diphenylmethane diisocyanate share by producer shown in *figure 6* (Linch and Linda, 2012).

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The primary technical consumption form of diphenylmethane diisocyanate is the polymeric diphenylmethane diisocyanate (PMDI), a brown liquid with a melting point of about $0^{o}C$ and a vapour pressure of < 1MPa at $20^{o}C$ (Sekizawa and Greenberg, 2000). Polymeric diphenylmethane diisocyanate is a mixture that contains 25-80% monomeric 4,4'-MDI as well as oligomers containing 3-6-rings and other minor isomers such as the 2,2'-isomer (Sekizawa and Greenberg, 2000).

Polymeric diphenylmethane diisocyanate is the form produced commercially from analine. Figure 7 shows the chemical structure of diphenylmethane diisocyanate.

Polyol

Polymers and monomers with multiple hydroxyl functional groups for chemical reactions are referred to as polyols. The number of hydroxyl functional groups in a molecule changes the nomenclature. For example, diols (dyhydric alcohols) have two hydroxyl groups in a molecule while triols (trihydric alcohols) and tetrols have three and four respectively. Polyether polyols and polyester polyols are the two main classes of polyols used for polyurethane manufacture. While polyester polyols usually provide excellent mechanical properties such as tensile strength, abrasion and wear resistance as solvent and oil resistance to the polyurethane in which they are used, polyether polyols provide high hydrolytic stability and good low-temperature flexibility. Polyether polyols are limited by poor resistance to degradation by ultraviolet radiation and oxygen when hot (Nextant, 2004). These limitations are usually overcome by both antioxidants and ultraviolet stabilizers. Hydroxy-polyethers are more used for the production of polyurethane than hydroxy-polyesters[1]. Polyether polyols are produced by alkoxylation with the starting materials either divalent glycols (ethylene, propylene and other glycols) or multivalent alcohols (e.g. glycerol, sucrose) and epoxides usually propylene oxide and ethylene oxide (Bousetad, 2005, Nextant, 2004). In the manufacture of polyfunctional polyols, glycerine, trimethylpropane, pentaerythritol, sucrose, sorbotol, water, bisphenol A, ethylenediamine, toluenediamine, ethylene glycol and propylene glycol are used industrially to supply active hydrogen (Nextant, 2004).

A REVIEW OF POLYURETHANE PRODUCTION IN NIGERIA

Nigeria is a big market for polyurethane producers. Mattresses producing companies are concentrated in Lagos, Kano, Kaduna, Portharcourt, Aba and Onitsha. Some of those companies are also cited in various parts of Ogun State, Oyo State and Kwara State. Each provides employment and gets revenue from the large Nigerian market. The major polyurethane producers in Nigeria are listed in *table*

Raw Material Sources for the Polyurethane Industry in Nigeria

The major raw materials for polyurethane production in Nigeria are currently being imported as there is currently no petrochemical company in the country producing either polyol or diisocyanates. These raw materials are being imported mostly from, China, USA, and Philipines (MarketsandMarkets.com, 2012). This is however not expected given the abundance of crude oil, which is the major source of the raw materials in Nigeria. The various petrochemicals produced in Nigeria have been surveyed and shown in *table 3*. The major challenge in polyurethane production is the total importation of the major raw materials as such plants are not built in the country despite the large market.

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CONCLUSION

The purchase of polyols , toluene diisocyanate and diphenylmethane diisocyanate from other countries by the Nigerian polyurethane manufacturers has grown significantly during the past few years. It is expected to keep growing at a rapid pace as long as Nigeria is not into the production of these products. The growth is mainly driven by a growing consumption in Nigeria. The demand for polyols, toluene diisocyanate and diphenylmethane diisocyanate in the market is fueled by demand from end-user industries such as construction, transportations, and consumer durables such as polyurethane foams which have a wide application in almost all areas of life. These include mattresses, foam insulation for appliances (refrigerators and freezers), home and automotive seats, elastomeric shoe soles, fibres (such as spandex) and adhesives.

Table 1. Typical components of polyurethane formulation

Chemical type	Reactivity to diisocyanates	Example
Polyol	Reactive	Hydroxyl-terminated reaction products of ethylene oxide and propylene oxide, with an initiator such as glycerol.
Chain extender	Reactive	Bifunctional short chain reactive molecules such as butane diol.
Cross-linker	Reactive	Polyfunctional low molecular weight amines or alcohols such as triethanolamine.
Blowing agent	Reactive	Water (producing carbon dioxide from the isocyanate–water reaction)
	Nonreactive	Carbon dioxide (as gas or liquid)
	Nonreactive	Pentane
	Nonreactive	Methylene chloride
	Reactive	Hydroxyl-terminated tertiary aliphatic amines such as triethanolamine
Catalyst	Nonreactive	Tertiary aliphatic amines such as dimethyl cyclohexylamine, diazabicyclooctane, N-ethyl morpholine
	Nonreactive	Stannous octoate
	Nonreactive	Dibutyl tin dilaurate
Surfactant	Nonreactive	Silicone liquids
Fire retardant	Nonreactive	Tris(beta-chloropropyl) phosphate (TCPP)
	Reactive	Propoxy brominated bisphenol A
Filler	Usually nonreactive	Glass fibre
	Nonreactive	Calcium carbonate
	Reactive, but insoluble	Melamine

(Allport, *et.al.,* 2003).

Nigeria, with its abundance of natural resources which include crude oil from which the major raw materials for polyurethane production can be synthesized for use by polyurethane manufacturers is not at all involved in their synthesis but spends huge amount in foreign

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exchange to import these chemicals. Nigeria being one of the highest consumers of polyurethane foams stands to save valuable foreign exchange and create employment opportunities if polyol, toluene diisocyanate and diphenylmethane diisocyanate are being manufactured in Nigeria.

The major challenge is the development of feasibility studies on the establishment of the factories for production of toluene diisocyanate, diphenylmethane diisocyanate and polyol and their implementations for the production of these materials for the polyurethane industry in Nigeria.

Table 2. Major Polyurethane Producers in Nigeria

S/N	Company's Name
1	Arco Foam
2	Bode Foam Industries Limited
3	Current Foam Industries and Chemicals Limited
4	Esco Foam Chemical Industry Limited
5	Euro Products Limited
6	Mouka Limited
7	Royal Foam Products Nigeria Limited
8	Sara Products Limited
9	Sharaton Foam And Chemical Industries Limited
10	The Unifoam Group
11	Vitafoam Nigeria Plc
12	Vono Products Plc
13	Winco Foam Industries Limited

Table 3. Petrochemical Companies and Refineries in Nigeria and Their Petrochemical Products

S/N	Name/Location of the Petrochemical Company	Major Petrochemical Products
1	Warri Refinery and Petrochemical plant	Polypropylene and carbon black.
2	Kaduna Refinery and Petrochemical company	Lube base oils, asphalt and waxes, linear alkyl benzene, benzene, heavy alkylate, kero solvent,normal paraffins, toluene, aromatic solvent, heavy paraffin, sulphur flakes
3	Portharcourt Refinery Company Limited	Fuels only. No petrochemicals produced.
4	Indorama Eleme Petrochemicals	Various grades of polyethylene and polypropylene
5	Escravos Gas-to-Liquid Project, Niger Delta	Converts natural gas to liquid fuels. No petrochemicals produced.
6	Natural Gas-to-petrochemical project Lekki	Production of methanol and its conversion to polyolefins.

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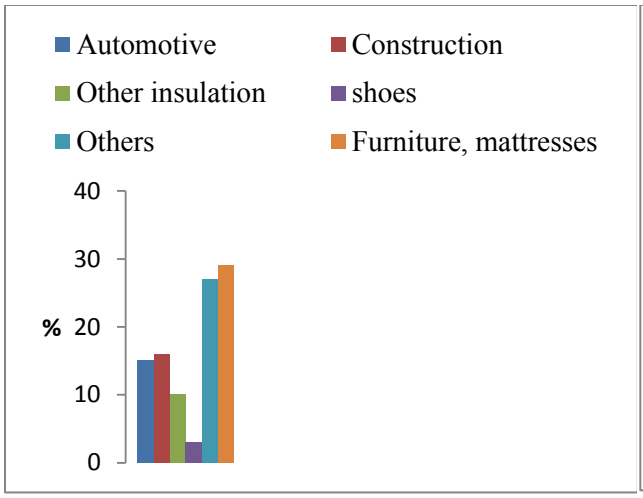

Figure 1: Polyurethane production based on application

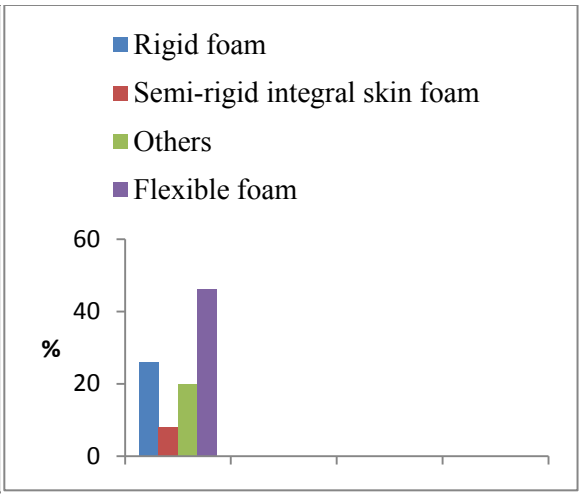

Figure 2: Polyurethane production based on the type of polyurethane (Allport, *et.al.,* 2003)

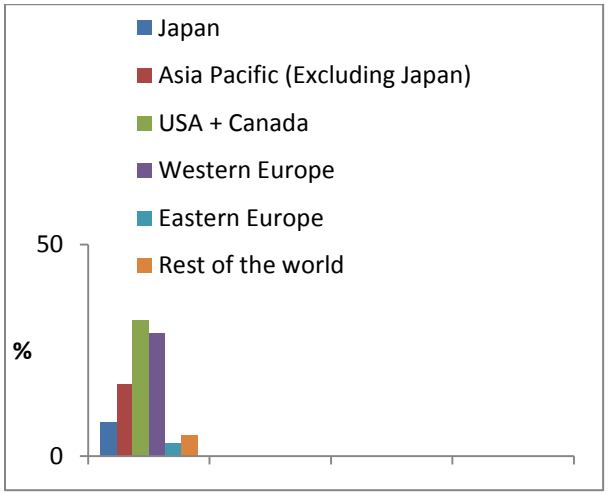

Figure 3: Regional production of polyurethane in 1998 (Allport, *et.al.,* 2003)

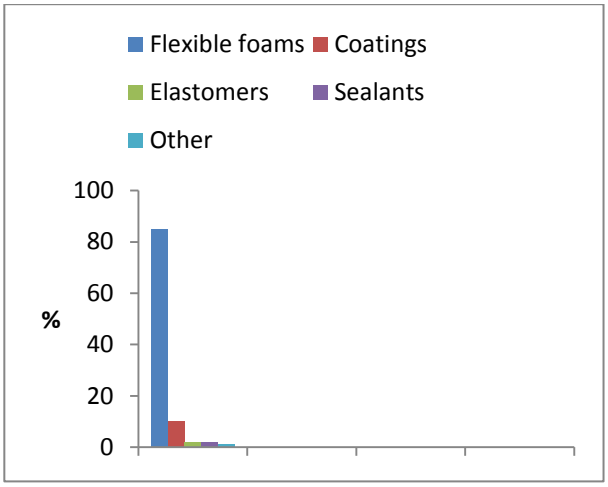

Figure 4: Global Toluene Diisocyanate Demand by End-Use (Nexant Chem Systems, 2008)

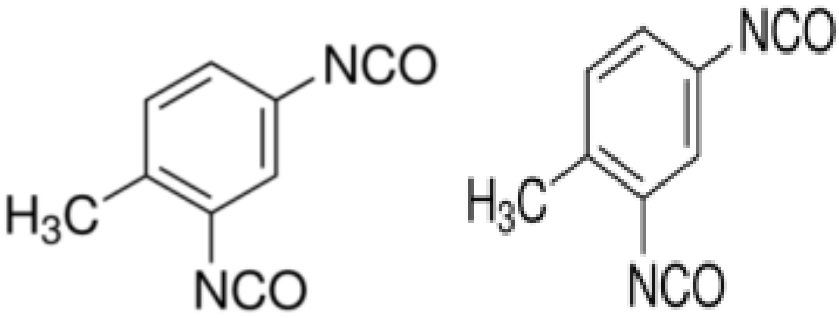

Figure 5. Structure of a) 2, 4- toluene diisocyanate b) 2,6-toluene diisocyanate

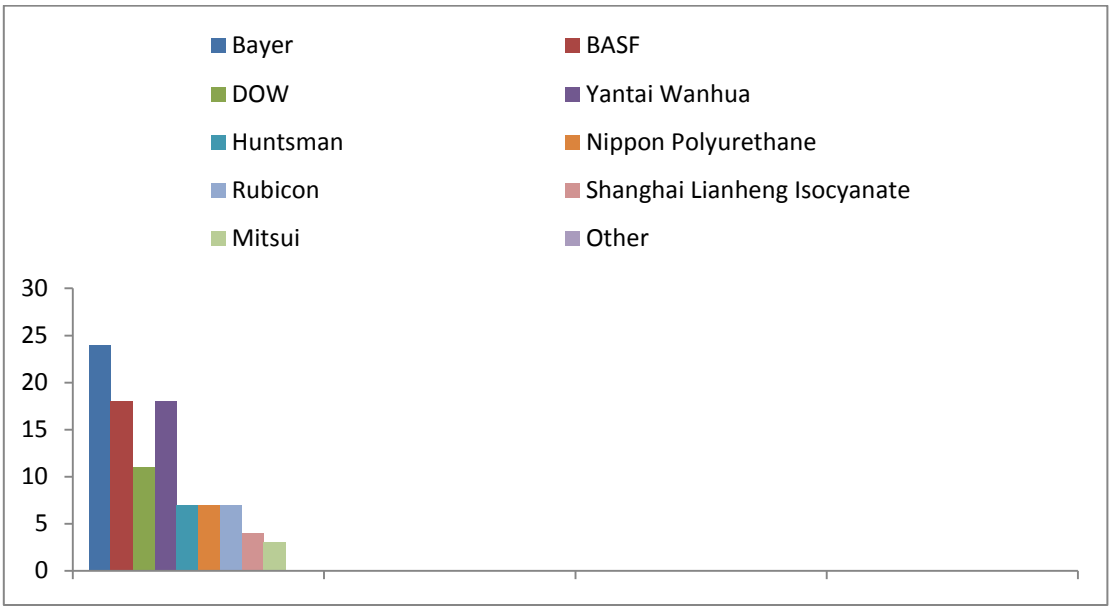

Figure 6. Global MDI capacity share by producer (Linch and Linda, 2012)

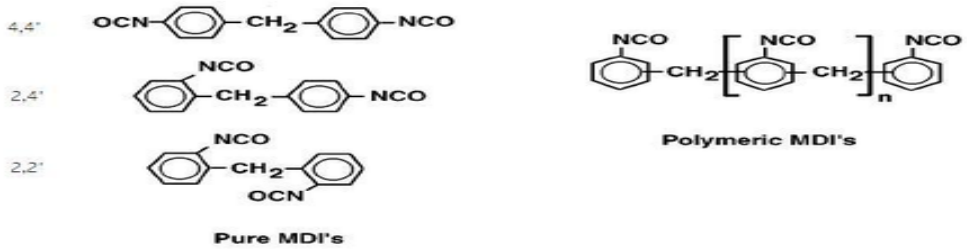

Figure 7. Chemical structure of MDI

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