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A Review on New Methods of Polyurethane Manufacturing primarily using Industrial Wastes

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Abstract: In a world where polymers are widely in demand and used in numerously, PU has its own vital role to play. They are used for making foaming materials, mattresses, paints, adhesives, flooring materials etc. in this paper, we investigate the various methods of utilizing the industrial wastes which is otherwise dumped off or has other adverse environment effects. Here, especially TDI (toluene di-isocyanate) tar from TDI manufacturing companies and PET (polyethylene terephthalate) waste are discussed. Effective methods to produce Polyurethane solely using TDI tar and also TDI tar and polyol recovered from PET wastes are included. Process like glycolysis, transesterification, etc. are included. Since the conventional PU , TDI , Polyol being very costly , This recycling and recovery processes are sure to bring down the cost and is an applaud able solution for solid waste management

Keywords: TDI-tar, Polyol, waste Recovery, Glycolysis, trans-esterification, reactivity, applications

I. INTRODUCTION

In topics petrochemical market, the importance of PU cannot be neglected. Over the years Polyurethanes have revolutionized the quality, providing safety, lightness, comfort and durability. Using polyol and Isocyanate compounds and by properly using other transformation processes by adding additives, we can obtain polyurethane ranging from flexible to rigid forms. They are mixed with metal, wood and other polymers and are not that visible as an end product , but we can undoubtedly see them every day in car, furniture's, pavements, walls, home, heating systems etc. Even when the advantages of PU are in numerous, there is a problem of high cost of its raw materials like isocyanates and polyol and thus the overall production cost becomes less economoical.in this regard, this paper looks upon a meticulous way to use up the industrial waste to adopt an economical way to manufacture PU. The industrial waste we process here are the TDI tar and PET wastes which are otherwise dumped or simply heated out in the environment.

The major focus in the paper will be the effective reuse of TDI tar into an efficient one sided or sole raw material to form PU or using it side by side with the recovered polyol from PET industrial waste. Thus the overall cost is reduced and also a proper way to avoid land waste and other negative aspects of heating up. All the explained processes are tested in laboratory and needs to be amended if for an industrial scale usuage.it can be mainly classified into the TDI treatment, polyol recovery and PU formation at last. Here these can also be used as individual products with many applications. Example is the scope of using the polyester polyol so obtained in better coating applications with melamine formaldehyde as curing agent.in total this papers looks in deep all the ways for a better and economical PU production using cheap and safer industrial waste pathway.

First the need of such a method is well explained by using real life examples of how and why these TDI tar and PET Wastes act in the environment. Any chemical plants sole aim might be to change raw materials to finished products, but here a new and much needed recycling and recovery from the waste is proposed for an environment friendly, yet an economical chemical process.

II. PROBLEM DISCRIPTION

The TDI tar which is a by-product of any toluene di-isocyanate manufacturing plant. TDI tar is indeed a very harmful by product or waste in many industries wherever TDI is involved in production. It's basically a black brown solid or a non-volatile residue component containing 10% to 30% (weight fraction) isocyanate group (NCO) brittle at room temperature. Heating at more than 200'c it becomes a very viscous liquid and more than 260, gases evolve, which is harmful for the environment. There are a shortage of method to utilize this product in a useful way and mostly these were dumped in pits under industrial waste.it is also been used as a heating energy source in India and Africa but it has many limitations including incinerator damage. The tar might adhere to the floor of the incinerator and it can be difficult to handle it as such. Also the limitation to not being able to be made into a uniform solution also is a major factor for an alternative way.

Coming to the next industrial wastes, Polyethylene terephthalate (PET) is an aromatic polyester. It has a great thermal and mechanical resistance and outstanding chemical properties. It is used in fibres, packing materials, and plastic bottles.

The main problem lies in its non-biodegradability.it is used in a very large scale and so the waste produced after its usage also persists. If we can actually recycle PET, it will help us to reduce the push on petrochemical products .For taking it's solvytic chain cleavage, hydrolysis, alcoholysis and glycolysis can be advised [1] .it is also noxious material which is resistant to biological agents .since all of this is produced industrially in a large-scale, its recovery or reuse is as important as any of the new chemical innovations and advancements.

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III. TDI TAR TO LIQUID TDI (CURING AGENT)

Owning to its main draw backs, the TDI tar has to be first converted into a molten or liquid form using chemical processes. Only after converting it into liquid TDI we can use it as a curing agent in PU manufacturing. The first step is to pulverize or break down this tar to a specific size range before going for further steps.it can be pulverized in a ball mill, colloid mill or disc mill accordingly.an important precautions to be taken here is that these processes and the upcoming mixing needs to be done in a complete anhydrous conditons.it is because the free isocyanate present and form gelation due to presence of water and thus all solvents needs to be dried. Aromatic solvents like anthracite oil or pitch oil can be used as its boiling point at atmosphere temperature is more than 200’c.the pulverizing temperature is when the TDI tar is a solid and can be carried out in room temperature itself. The time of pulverization does depend on properties of tar, solvent used, capacity of mill etc. but generally we take up to 1-10 hours. Concentration needs to be duly 40% in the end liquid TDI, so by back calculations, the ratio of TDI tar in the solvent to that of the weight of the tar can be kept 1.5:9 [6].

Next step is the adding of aromatic solvent into the liquid TDI. It is mixed in a specific dissolving temperature. Either of the below said methods can be used. TDI tar after pulverizing is poured into aromatic solvent can be held at a temperature higher than 200’c and then it’s mixed with stirring. In another method, it’s poured into solvent at a temperature lesser than 200’c, then its kept at a temperature more than 200’c and kept for 5 minutes. Solution so obtained is cooled. This can be used as the curing agent in the PU manufacturing process. This TDI tar has good reactivity with hydroxyl and amino groups. polymeric compounds like PPG and aniline etc. to form two package paints, road paving compositions, adhesives, foam and flooring materials. But here our main area of interest is to use this so formed liquid tar as curing agent for PU formation.

IV. ISOCYANATE REACTIVE TAR (BASE COMPONENT)

In this process we cannot use the TDI tar as such. We need to have isocyanate reactive tar so that it has greater affinity for the reactions and for this, special processes needs to be done. We react tar with formaldehyde in the presence of a basic catalyst and a phenol is added as activator

When coal tar reacts with formaldehyde, its reactivity is very less and so they cannot be used. But when we use it with TDI tar the hydroxyl group content is increased and thus it has more reactivity. Formaldehyde can be used in a weight ratio of 2.25 parts by 100 parts by weight of tar.

We use formaldehyde. bases which we use can be either amines or aqueous ammonia (28%).if its ammonia, 5 to 10 parts of it to 100 parts of tar can be used and if its amines a mole concentration of 1-8% can be used.to increase the hydroxyl reactivity we add phenol. it can be premixed with tar or together with tar and formaldehyde by weight ratio of 25 parts by 100 parts of tar. The temperature can be kept between 80 to 120 ‘c and time of 1-8 hours. This can be varied accordingly to the scope of our products, [6] but for a general reproach, these parameters are used as such. After this mixing, the water, catalyst, unreacted substance is removed for a distillation at reduced pressure at more than 100’c.

Thus the liquid TDI so produced in the first step is used as a curing agent and isocyanate reactive tar as a base component obtained in step 2, we add both and other chemicals to it to obtain polyurethanes. This will be discussed in the paper in a later stage.

V. RECOVERY OF POLYOL FROM PET WASTE

We recycle the waste PET to form polyester polyol merely by glycolysis of waste by PPG (Polypropylene Glycol) followed by trans-esterification by castor or jatropa oil. The process is explained below in detail.

The first step is the glycolysis of the PET waste using PPG. For an experimental set up we can use a three necked reaction kettle with a stirrer and a condenser. Industrially we can use a stainless steel jacketed reactor (0.1 to 10 m3).on top, a demister, distillation column and a heat exchanger needs to be instilled. There is a need of stirring at high speed (agitated stirrer vessel).in a multiple inlet system for nitrogen inlet and a feed and PPG inlet. Bottom value is then sent to filtering unit. Temperature is generally controlled via an oil heater. We add PET waste and PPG (2000 molecular weight) together in this reactor. Zinc acetate (0.5%) is added as the catalyst. Temperature can be set to 180’c and a time of 1 hour or accordingly. Heat it to temperature more than 210’c until all solids disappear. It’s finally milled to 2 to 8 mm size [3].

Next step is to react this oligoesters so formed above for trans-esterification so that saturated hydroxyl polyester polyol can be formed. These products are reacted with castor/jatropa oil with weight ratio 1:10.these oils are both available in companies in India (Gujarat).DBTDL (dibutyl dilaurate-2wt %) is used as the catalyst.it is carried out in a same reactor type. It needs to react without vacuum heating it to 80’c and later with vacuum of 125 mm hg, it’s heated for a total of 1.5 hour[5].As these processes are carried out, we get the saturated hydroxyl polyester polyol and this has in numerous applications.one such example of an efficient application is for coating materials . The polyester polyol so formed can be made a base component with melamine formaldehyde as curing agent with a weight ratio of 1:1 can be used for coating on mild steel panels. Thus a better coating material is so obtained [4]. All tests including MEK double rub and pencil hardness test, dip test has shown better performances, to an extent even corrosively resistance was also seen as reduced.

Using this so formed polyol, PU can be manufactured. These PU has a netter flame retardancy, long shelf life, low acid content.it has a better thermal coefficient, insulation factor and even a 20% higher compression strength.it is discussed in detail in the next session even with the additives to be added.

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VI. POLYURETHANE MANFACTURING

Pu (Polyurethane) is formed by a combination of polyol and di-isocyanates.it is used to produce paints, adhesives, flooring and foaming materials. here we see the proposed method of manufacturing pu using recovery and reuse of waste products. this waste products include tdi-tar and pet wastes. exclusively from tdi-tar: using tdi-tar was waste, we had processed liquid tdi and in replacement of polyol, we use the isocyanate reactive tar manufactured using the same tdi tar. from tdi tar and waste pet :we use the processed liquid tdi tar as curing agent and the polyester polyol obtained by the recovery process of pet waste. be it either of the processes, polyol/isocyanate reactive tar is kneaded by a ball mill, mixer, and kneader and then appropriate additives etc. are added into it in the reaction using multi inlet.

Curing catalyst like dibutylin dilaurate (accelerator) and phenols (retarders), fillers like talc, clay, mica, diluents like dibutyl phthalate, solvents like aromatic hydrocarbon like toluene , resins like petro resins, drying agents like calcined gypsum and bituminous like coal tar, asphalt are used[2]. The type of feeding in a reactor to produce PU is explained by the figure below.

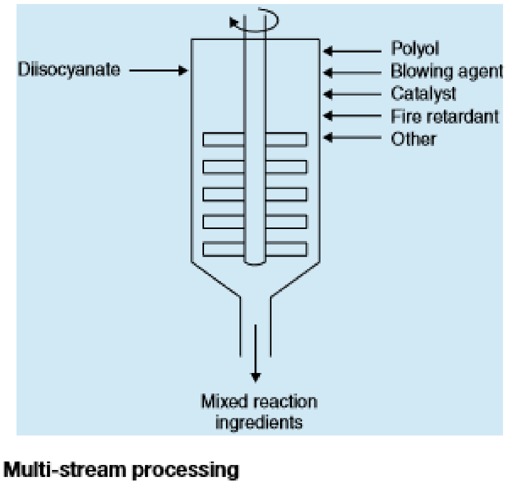

Fig 1. A typical example of a PU manufacturing feeder

VII. CONCLUSION

This method of utilizing the byproducts to a highly valuable product indeed opens a new and great market for polyurethane products. It even removes the harmful effects of all these side products.by this devised method, the waste PET is put in proper use and also TDI tar.in any chemical plant where these are a matter of concern, if processed accordingly forms a loop wherein the adverse effects on the environment is minimized .as we know the bottles and packaging materials of PET is increasing in an exponential rates. With the current population needs, it will continue to expand.in such a scenario, if we can recover a valuable and useful product by adding a few more chemicals, the mere extra processes are well justifiable. Here we saw the proper usage of the PET wastes and TDI tar proved to be an even more success as it can act as the sole role material for PU formation even by replacing the polyol required. The scope of such a method is revolutionizing to a great extent.

This paper has looked two of the main applications and methodologies to go on for PU manufacturing. The industrial wastes are put into proper use and made profitable and safer at the same time. Paper has concentrated more on the academic research than in an industrial scale but gives an apt example of how and why these should be highly employed in day to day industrial life very fast. The technologies present are well sufficient and with a little extra vison and a few additives, the applications of such a method as this, it's endless. The sofa we sit in, materials used in our car, the wall, paints, pavements, skid free skates etc., everything is an application to this concerning PU.This paper has thus made an attempt to reduce the gaps present in the recycling and reuse of a few industrial wastes .it is a debate less fact that in future, this method is going to be used up in high scale in industries and also more advanced technologies of the same are expected to be proposed.

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