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Retardant N- Nitrozo Diphenyl Amine

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ABSTRACT

Retardant (N- nitrozo diphenylamine) is considered as one of the important raw material Which is used in some rubber blend.Use as a vulcanization retarder during rubber processingfor controlling of plungerinjectionas well as being a plasticizer[1]. In this research the substance has beenprepared in laboratoryand also in small unit (7 tons per year). Then comparison it with commercial samples by two directions ,The first is represented by different physical and chemical properties tests such as (density, solubility , melting point, infrared rays and others) The second direction is represented by using prepared and commercial samples each one alone in certain rubber mixture then do sometests on the rubber production as a tensile strength, elongation and hardness.Follow the evolution of specifications for rubber samples by using curing measures (scorch time, curing period , over curing) and the most common of these measurementsthrough the oscillating Disk Rheometer tests[2],All tests give good results.

Key words: Retardant, N- Nitrozo Diphenyl Amine, plasticizer.

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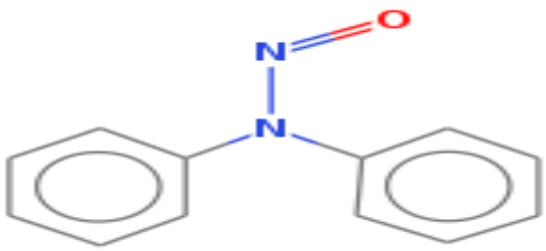
INTRODUCTION

Sulfur is one of the most important crosslinking agents[3]. It helps in the chemical bonding between the rubber chains when mixing and heating to the desired thermal level. This condition is known as vulcanizing. This affects positively the specifications of the product and increases the tensile strength, the strength of the tear, tear resistance, hardness, stress strength, friction force, etc.[4]

In addition to sulfur,hydrogen peroxide is used as a crosslinking agent.The retarder used as an additive material to the rubber mixture during thermal forming process, using the rubber injection machine and the most important materials used such as, Phthalic anhydride. N - nitroso diphenylamine which is the subject of our current research and there are many other materials added to the rubber mixture according to the required properties of the product.

MATERIAL AND METHODS



N- NITROSODIPHENYL AMINE

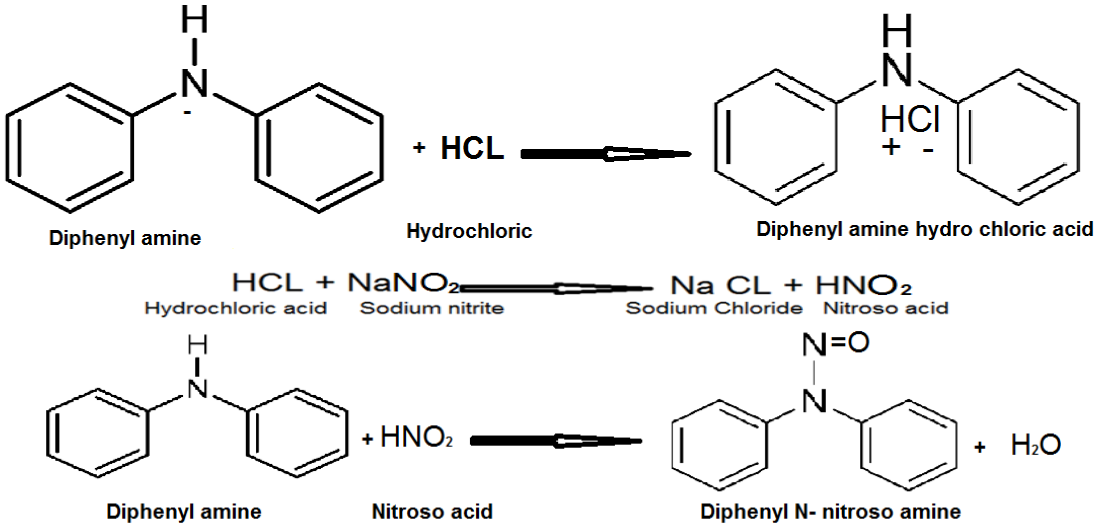
Practical part: Thispartof the research includes laboratory and pilot unit preparation

Lab. Preparation[4]:

dissolved (17 g) of di phenylamine in (170 mL) of warmethanol with stirring. thenadd (12 ml) of concentrated hydrochloric acid to the solution prepared in the previous step gradually with continuous stirring to form the di phenyl amine - hydrochloric compound.Prepare of sodium nitrite solution ($NaNO_2$) by dissolving (8 g) of sodium nitrite in (12 ml) of distilled water with continuous stirring until the completion of dissolving.Pouredrapidly the sodium nitrite solution into the di phenylamine-hydrochloric solution with constant stirring, where the di phenyl-N-nitrosamine compound is produced directly . leave the reaction in ice for 4 minutes and then filter off the yellow crystals which have separatedby a Buchner funnel and washed several times with distilled water to remove sodium chloride salt from the reaction. Resulting material will be dried using an oven at a temperature of 50 °

Mechanism of the reactions:

The mechanism of the reaction can be clarified through the following equations:



From the above equations, we observe that the basis of the reaction is the formation of nitrous acid (HNO_2) simultaneously through the reaction of concentrated hydrochloric acid (-HCL) with sodium nitrite ($NaNO_2$). The final reaction between nitrous acid (HNO_2)anddi phenylAmine.

Pilot unit preparation[*]:

The retarder material wasprepared in the reactor shown in (Figure 1) by dissolving (5 kg) of di phenyl amine in (50 liters) of solvent used (ethanol) with constant stirring for 2 hours. Then adding concentrated hydrochloric acid gradually.
During this process, sodium nitrite solution prepared by dissolving (2.5 kg) of sodium nitrite with (3.5 liters) of water and stirring until the solubility is complete. Then sodium nitritesolution is added directly to the main preparation reactor after finishing acid added.

Continue mixing for a period of one hour and then filter the resulting compound and wash several times with water until the sodium chloride salt is removed from the preparation.

Then the material is dried at a temperature of (50°C) and packing.The sequence of preparation steps can be followed from the (Figure 2)below.

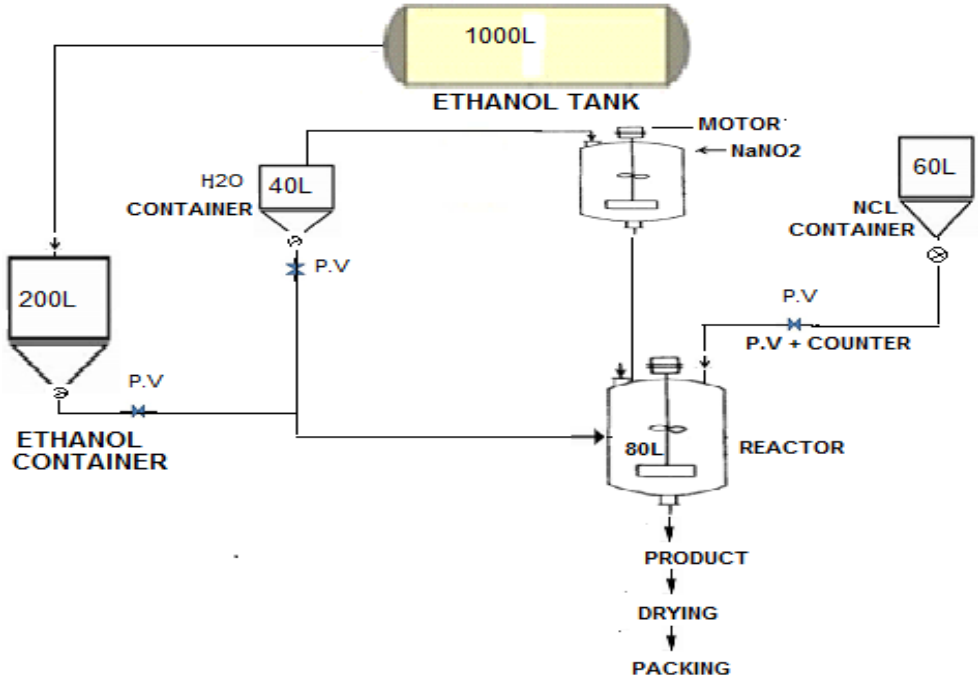


Figure 1: Production unit[9]

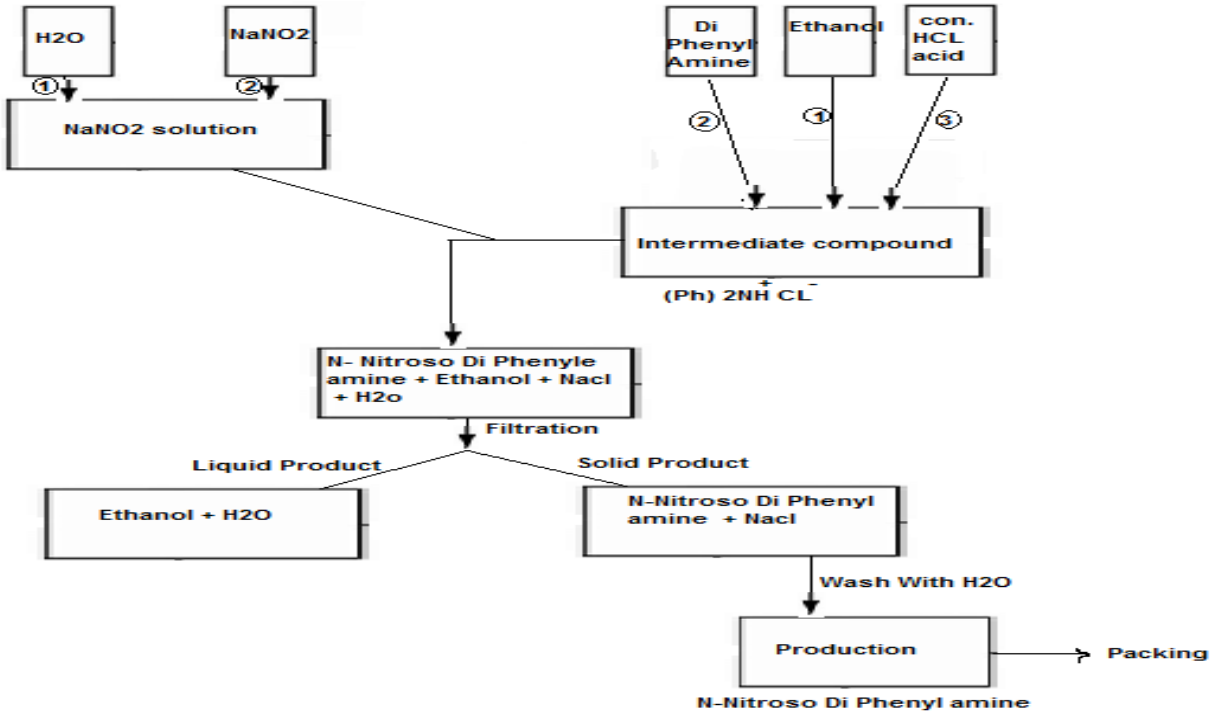


Figure 2: Product preparation steps

RESULTS AND DISCUSSION

1- Laboratory tests:

A) Physical and chemical tests:, Five samples were prepared , measuring the chemical and physical characteristics and compared them with the commercial samples , as shown in the (Table1) below,Obtain a similar resultin solubility with different solvents[5] , melting point, density[6] …etc .

Table 1: Physical and chemical tests of prepared samples

Samples	1	2	3	4	5
Color	Yellow-Brown	Greenish yellow	Yellow	Deep green	Yellow
Melting point (°C)	63	60	65	\ 62	\ 67
Densityg/cm³	1.35	1.32	1.3	1.3	1.34
Solubility bybenzene	Soluble	Soluble	Soluble	Soluble	Soluble
Solubility by gasoline	Slightly soluble	Slightly soluble	Slightly soluble	Slightly Soluble	Slightly soluble
Solubility by CCL4	Soluble	Soluble	Soluble	Soluble	Soluble
Solubility by acetone	Soluble	Soluble	Soluble	Soluble	Soluble
Solubility by ethanol	Soluble	Soluble	Soluble	Soluble	Soluble
Solubility by water	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

B) Diagnosis by IR spectrum[7] :

When using infrared spectrumof nitrosamines compoundsobserve two absorption bandscorresponding to N = O stretching vibrations. One of them is of a 1486—1408cm. - 1 ,give a strong band offrequency between 1106 and 1052 cm."1, which should be assigned to N — N stretching vibrations of the group > N — N = O. and other bands, Sowhen compare the bands between infrared spectrum ofprepared and commercial samples as shown below in (Figures3,4).observea perfect similar and clear indication of the chemical composition of both samples.

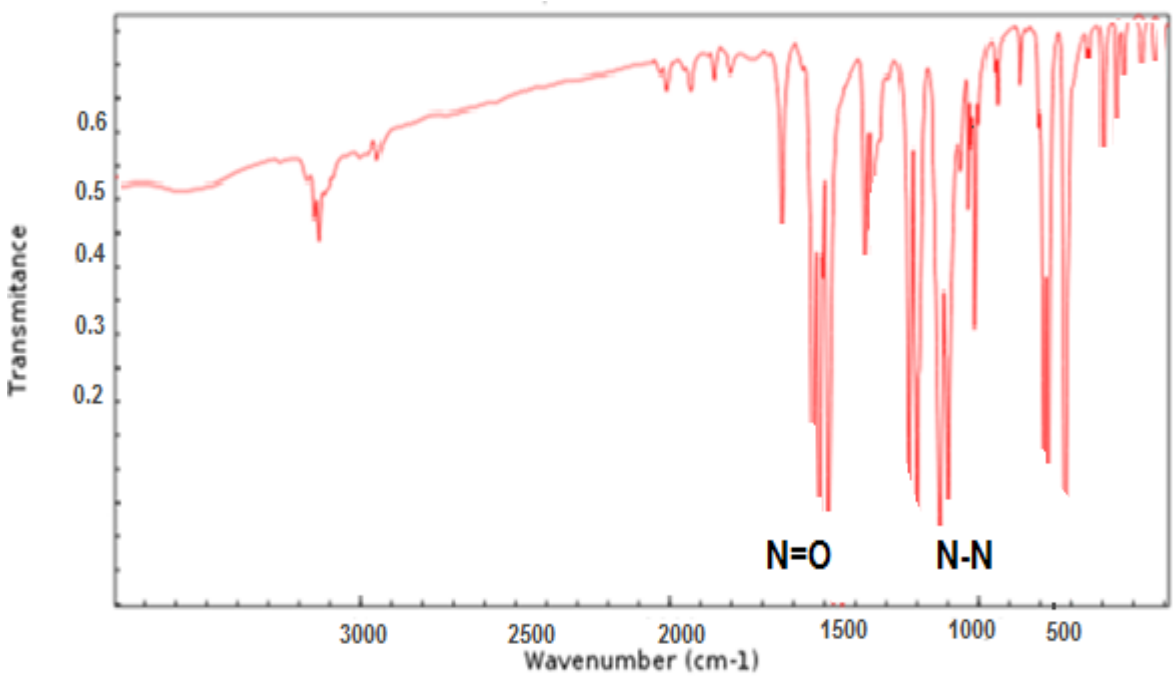


Figure 3: IR spectrum of the imported sample

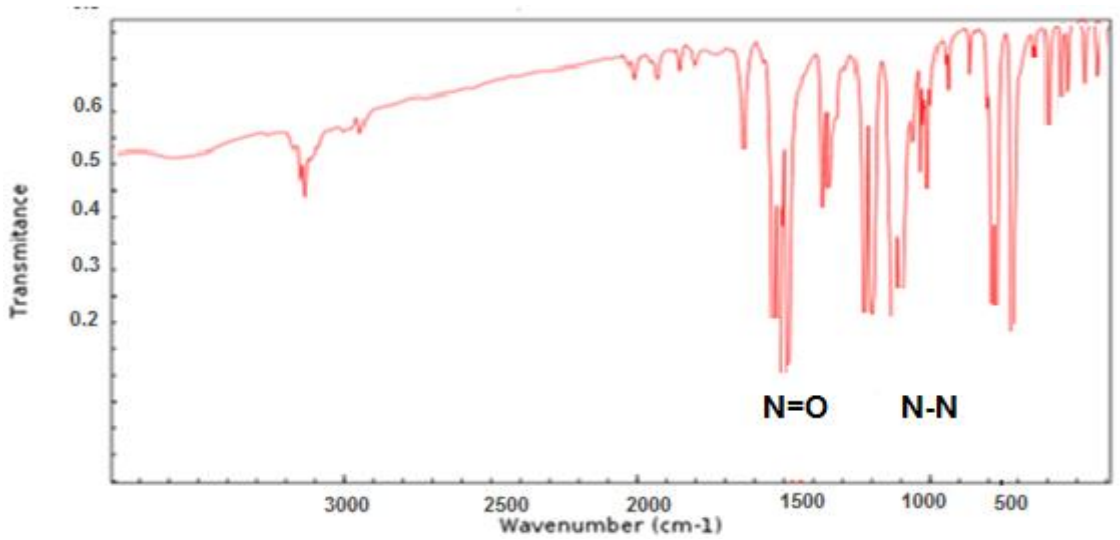


Figure 4: IR spectrum of the prepared sample

2- Mechanical tests of rubber mixture[8] :

Add prepared and commercial samples (each separately) in a certain rubber mixture type (SMR62)[**] (Table 2) below,Then conduct some standard tests on the product.

Table 2: Rubber mixture (SMR62) composition

substances	Chemical form or symbols	%
Natural rubber	**SMR**	**100**
Active	**Zno**	**10**
Active	**Stearin**	**1**
Antioxidant	**4010Na**	**1.5**
Antioxidant	**H**	**1**
Softness	**Oil**	**5**
Accelerator	**Cz**	**0.8**
Accelerator	**Dm**	**0.1**
Crosslinking agents	**Sulphur**	**2.2**
Retarder A	**NNDPA**	**0.05**

These tests included the following: - 1 - Tensile strength 2 - Elongation 3-HardnessTensile strength is important for a material that is going to be stretched or under tension ,is in units of force divided by units of area usually N/cm2 . When tensile stress is considered ,the sample deforms by stretching , because longer . This is called elongation , usually about percent elongation unit , Is just the length of polymer sample after stretching per original length multiplied by 100 , (L / L_0 x 100), Hardness tests (ISO 7619-1 (Shore A)normally involve the quantitative assessment of the resistance to penetrations of a material by an indenter As we observe below (Table3) there is no negative effect of retarder work on the final specifications, but only to delay the start of crosslinkprocess and facilitate the injection process and compression.

Table 3: Mechanical testing of prepared samples

Samples	tensile strength N/cm2	Elongation %	Hardness Shore A
Sample (1)	234	660	56
Sample (2)	232	645	55
Sample (3) Commercial	240	670	57
Sample (4) Commercial	238	650	57

3 - Rheometertest

This test gives a clear indication of the retarderwork in the rubber mixture during the vulcanization stages. The curve below shown in (Figure5) Three stages of the product. The first stage (A) is called scorching time.Refers to the past time before the crosslinking reaction start,so it must be long enough to allow,mixing, manufacturing, molding and flowing of the rubber blend in the mold before vulcanization.It is the primary stage of heated rubber dough.

- The second stage (B) is calledcuringPeriodis the treatment or vulcanization stage.The first section represented of the flowing state that is generated by the heat, while the second section is the largest crosslinking reaction.

- The third stage (C) terminate of Vulcanization.This period is related to the final physical properties of the product.(ASTM D-2084)

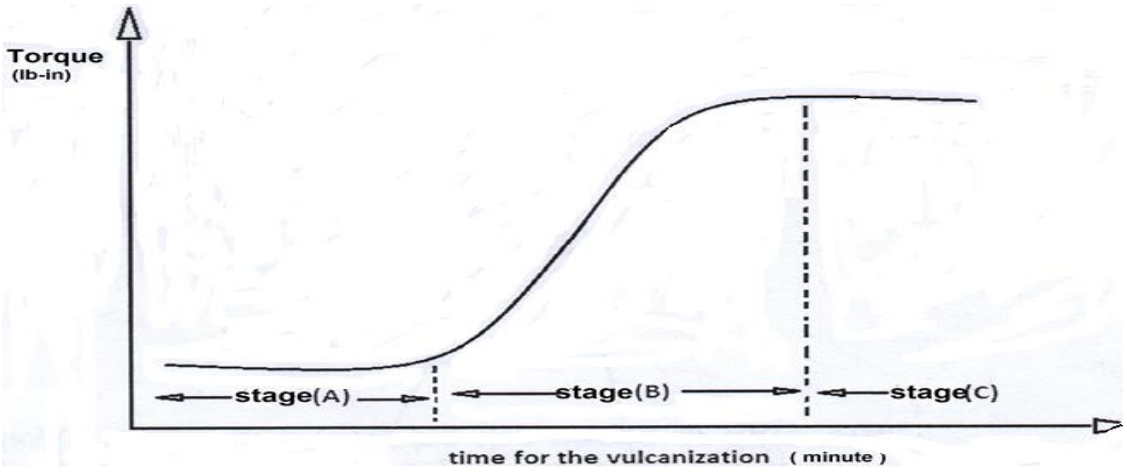


Figure 5: Vulcanization Stages[9]

(Figure 6) shows three graph curvesrepresenting the blendsrubber, The(curve 1) for the rubber mixture by using 4% of the prepared retarder .the curve (2) for the rubber mixture by using 2% of the prepared retarder and the curve (3) by using 2% of the commercial retarder.

Through the added ratios of the samples below, we observe that scorching time ofmixture No. (2 and 3) is approximately similar, while there is a clear increase in mixture (1).Increasing of the primary stage of heated rubber dough gives theenough time to convert it into a thermally homogeneous dough (60-70 ° C) inside the injection tubes before injecting it into the molds to complete the vulcanization process.[8]

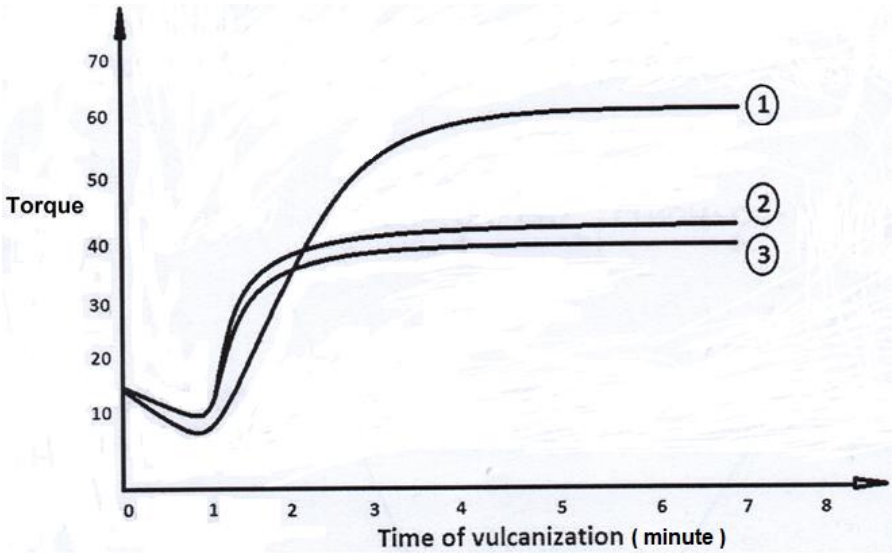


Figure 6: Vulcanization time for different samples

CONCLUSION

The mechanism of retarder work and its effective in the mixture rubber is not known accurately,thereweresome researchers shows that its effective by preventing the binding of sulfur with polymer , Also effect on the accelerators added, and others went to the effective on stimulants Additives for rubber mixtures such as zinc oxide and many other factors.(5)

The results showed the apparent effect of the retarder work in the rubber mixture by delaying the crosslink process and increasing the time period preceding the vulcanizing process. This will give in greater thermal homogeneity of the dough inside the feeding tubes installed on the injection machines. In addition to the fact that the retarder is a plasticizer material, it facilitates the injection process from the feeding tubes to the press molds where the process of vulcanization is done in different temperatures and pressures depending on the quality and specifications of the required product. Without the retarder, the injection process cannot be performed properly, many problems affect the work of the machine.

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