

## IMPROVEMENT THE STABILITY OF UNSTABLE POLY NITROESTER BY DIETHYL DIPHENYLUREA

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### Abstract

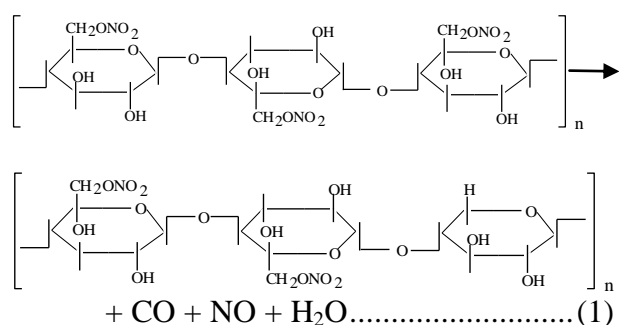
New methods were developed for treating of an unstable poly nitroester (Nitrocellulose based composition) by extracting the harmful decomposition products formed during the storing time and substituting the loose in diphenylamine (DPA) as stabilizer content in poly nitroester formulations using diethyl diphenylurea, good stability results were obtained after treating three types of unstable poly nitroesters.

### Introduction

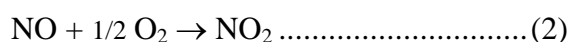
For many years following the invention of nitrocellulose by Schonbein and Pelouze in 1846, the lack of stability of this product was to remain a serious problem to manufacturers. However, many works and researches were carried out about the stability of nitrocellulose and was found that most nitroesters, such as nitrocellulose and nitroglycerine are saponified with time. The saponification is accelerated by the formation of nitrogen oxide in combination with heat, moisture and light.

Nitrocellulose (NC) breaks down autocatalytically to yield acid decomposition product which accelerate the decomposition rate once decomposition has started and may in certain cases produce spontaneous ignition [1].

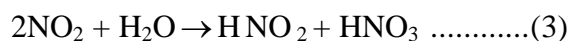
Generally the chemical decomposition of nitrocellulose can be illustrated by the following equations [2]:



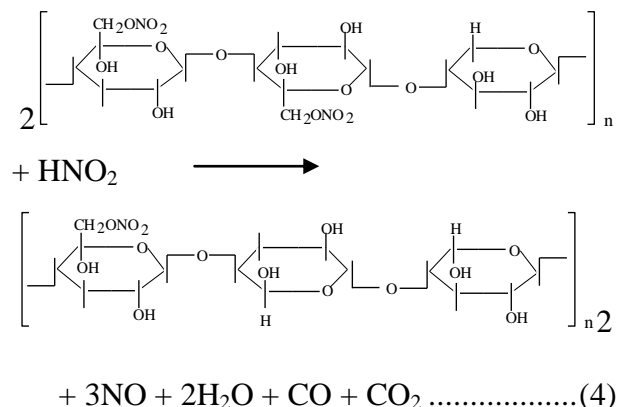
The presence of oxygen in atmosphere will oxidize the nitrogen monoxide to nitrogen dioxide which has brown color and special odor.



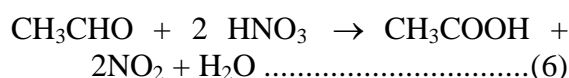
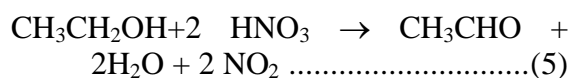
With the assistance of moisture in poly nitrate ester and that present in the atmosphere, the nitrogen dioxide is converted to nitrous acid and in many cases to nitric acid:



In this case, nitrous acid will react with the organic compound according to the following equation:



The nitric acid liberated according to equation (3) will attack the volatile ethanol which were added during the manufacturing of the poly nitrate ester according to the following equations: [3]



The spontaneous decomposition of nitrocellulose in the air produces nitrous and nitric acid which promote a farther decomposition. If nitric products however, are removed continuously, the uncatalyzed

decomposition is extremely slow, Poly nitro ester may be stabilized by the addition of substance which reacts with these acids and removed them, provided neither the substance it self nor the products of its reaction with the acid attacks NC [4].

Stabilizers react with nitrogen oxides that formed from the decomposition of nitrate esters and eventually non catalytic products are formed, so that auto catalytic decomposition is minimized. In this way the chemical stability of the nitrate esters increases, but the content of stabilizer decreases [5].

Diphenylamine is used as stabilizer for poly nitro ester. It reacts with nitrogen oxides. As a result, mainly N-nitroso, mono, di, and to a minor extent trinitro-diphenylamine and mononitro-N-nitroso diphenylamines will form [6].

Investigations have shown that the basic properties of DPA are so weak that can hydrolyze NC, but they are sufficient to neutralize any acid product arising either from the decomposition of impurities in the nitrocellulose, from the oxidation of residual solvent or even from decomposition of NC itself.

It was also demonstrated that the basic properties of DPA may have a deleterious effect on the nitrate esters if the DPA content exceeds 5% so, the best stabilizing result are achieved by using 1-2.5 % DPA.

Diphenylamine chemically binds the evolved decomposition products of nitrocellulose and consecutive products with an increasing degree of nitration are formed. Hence, consecutive nitrated products of DPA, from the N-nitroso-DPA and the mono-nitro-derivatives of (DPA) to the hexa-nitro-derivatives of (DPA) are formed with time. Some of them, N-nitroso-DPA and mono-nitro-derivatives of DPA, also have a stabilizing effect.

As can be seen in Fig.(1), the concentrations of N-nitroso-DPA and mono-nitro-derivatives of (DPA) increase with increasing aging time. Since these (DPA) derivatives have an important stabilizing effect, they concurrently with the remaining (DPA) react with the NC decomposition products in a further step. When the (DPA)

content becomes sufficiently small, the reactions of the (DPA) derivatives prevail, because the chemical accessibility of the unreacted (DPA) becomes a limiting factor. Then, diphenylamine depletion does not depend on its concentration. [7].

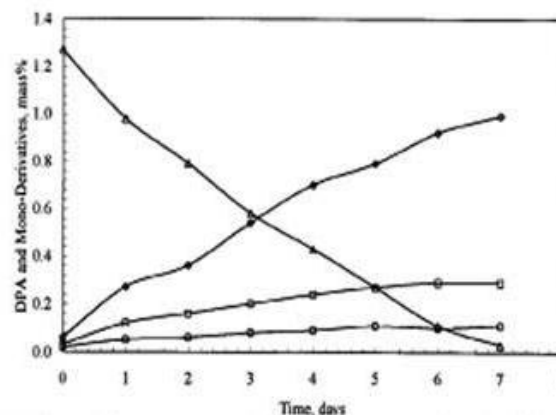
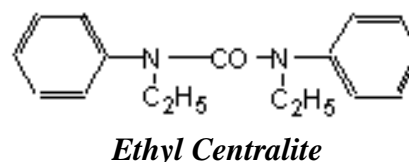


Fig. (1): Major stabilizer components in poly nitroester as a function of time of aging at 90 °C.

Centralite I, symmetrical diethyl diphenylurea. It is used as a stabilizer, gelatinizer, and waterproofing agent. Ethyl Centralite can be used in relatively large proportions (up to 8%) of the poly nitroester composition. It was successful use as a stabilizer and "non-volatile solvent". [8]



The aim of this paper is to select unstable nitroesters Table (1) and treated in different methods, some of them used to remove the harmful decomposition products and the others to substitute the loose in the percentage of the residual (DPA) in nitro ester using ethyl centralite.

## Experimental Part

### Apparatus and Equipments

- Circulation bath with operating temperature from 45 °C to 300 °C.
- Column of borosilicate glass with the following dimensions:
  - Inner diameter 45 mm.
  - External diameter 49 mm.
  - Length 400 mm.

### Chemical solutions

A solution of 1.0 % w/w (Ce) in ethanol and water (80g Ce+200g ethanol+7720g water), Table (1) contains the unstable nitroesters which were used.

### Recommended treating methods

Two different treating methods were used as follows:

**1-Soaking method:** This method was used to extract the decomposition products from poly nitro ester after soaking in water as follows:

A weighed quantity of an unstable poly nitrate ester was placed in to the circulating bath filled with about 6 liters of distilled water.

Poly nitroester was treated at different temperatures in the range (35-95 °C).Drying the samples were carried out at 50 °C.

**2-Treatment with (Ce+ Ethanol+ Water) solution:** This method aims to substitute the loose in the percentage of the residual DPA in nitro ester using ethyl centralite .This process was carried as follows:

A weighed quantity of unstable poly nitroester is placed in the column after being joined the circulator with the column. The quantity of distilled water is allowed to stand in circulator bath .Setting the temperature at 70 °C and the flow at available maximum rate[(80-85) cm<sup>3</sup>/sec], after the temperature reached the setting degree, the solution of Ce-Ethanol was added gradually in the circulator bath.

## Results and Discussion

### Soaking Method

In spite of the simplicity of soaking method, many factors which affect soaking process must be optimized .These factors depend on the type and dimensions of nitroester and hence, two factors are seemed to be very important and must be studied.

The first factor is the temperature of water which is used for soaking and the second factor is the soaking time.

### Soaking of flake type

Unstable poly nitroester was treated at different temperatures(30,50,70,90,and 95°C) at a constant time (2 hours).The results for this

treatment is presented in Table (2) which shows that the best temperature to be used is 90°C.To study the effect of time the samples were soaked for 2,4,6,8 and 10 hours at 90°C, the obtained results are shown in Table (3) which indicate that soaking time dose not show any effect on [H.T] and [B.J] tests.

### Soaking of tubular type

Similar experiments were carried out on this type at the same way which was previously done for (flake) type. The range of temperature was up to 70°C because higher temperature is inadvisable because the nitroester will be of high porosity. Table (4) shows the obtained results which indicate quite obviously that 70°C is the best temperature to be used.

The effect of soaking time was also studied, Table (5) shows that the treatment time within two hours is quite sufficient to give an improvement in the stability results at the recommended temperature.

### Soaking of cylindrical type.

This type was treated at the same manner as indicated in tubular type, The results of soaking samples are listed in Table (6) and Table (7) for temperature dependence and time dependence table shows that neither (H.T) nor (B.J) stability tests gave an improvement in stability results, this means clearly that soaking process unable to remove the harmful products from this type.

### Treatment with (Ce+ Ethanol + water) solution

#### Treatment of cylindrical type

This type was treated with 1.0 % (Ce) solution using a special column.

The method of treatment occurs is different from the (flake or tubular).The shape of cylindrical type allows the use of fluidizing technique inside the column and by increasing the flow rate to about (80-85) cm<sup>3</sup>/sec a good mixing has been obtained.

When 200g of poly nitroester was treated with 1.0 % (Ce) solution with a variable time of treatment (1.0,1.5 and 2.0 hours)a good improvement was obtained in the stability tests (H.J and B.J) which reveals the effect of increasing stabilizer content inside the nitro ester .Table (8).

### Treatment of flake type

This type was treated with 1.0 % (Ce) solution with .The treatment was done using the same column Because of the geometrical form (flake) this type was treated inside the column as a fixed bed .Table (9) shows the results which were obtained from the treatment of 150 g of this type which indicate that there is a good improvement in the stability results.

### Treatment of tubular type

This type was treated at the same manner as indicated in flake powder .The results is presented in Table (10) which also indicate that there is a good improvement in the stability results.

**Table (1)**

**Chemical properties for the selected Flake, Tubular, and Cylindrical types of Poly nitroesters.**

Type of nitro ester  Test	Cylindrical		Flake		Tubular	
	Recommended data	Recorded results	Recommended data	Recorded results	Recommended data	Recorded results
DPA content (%)	1.2-1.8	1.04	Min.1.00	1.18	1.20-1.80	1.28
Stability Test :						
Heat test at 100 °C (appearance of brown fumes)	Must not appear before 7 days	5 days	Must not appear before 6 days	5 days	Must not appear before 7 days	6 days
Bergamnn-Junk test at 132 °C (ml of NO/5g nitro ester )	Max. 11.0	9.31	Max. 15.5	14.02	Max.11.0	8.92

**Table (2)**

**The effect of temperature on soaking flake type Poly nitroester.**

Water temp. °C	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	Residual solvent content %
30	5	10.20	0.91	0.42
50	5	10.62	0.95	0.37
70	5	9.00	0.97	0.40
90	5	7.92	0.87	0.29
95	5	7.92	0.73	0.31

**Table (3)**

**The effect of time on soaking flake type Poly nitroester at 90°C.**

Time ( hrs)	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	Residual solvent content %
2	5	7.92	0.87	0.29
4	5	7.38	0.81	0.27
6	5	7.56	0.90	0.22
8	5	7.32	0.91	0.23
10	5	7.21	0.92	0.20

**Table (4)**

**The effect of temperature on soaking tubular type Poly nitroester.**

Water temp. °C	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	Residual solvent content %
30	6	8.81	0.87	0.42
40	6	8.69	0.92	0.39
50	6	8.50	0.89	0.40
60	6	8.65	0.93	0.37
70	6	7.65	0.81	0.35

**Table (5)**

**The effect of time on soaking tubular type Poly nitroester at 70°C.**

Time ( hrs)	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	Residual solvent content %
2	6	7.65	0.81	0.35
4	6	7.70	0.87	0.40
6	6	7.61	0.90	0.32

**Table (6)**

**The effect of temperature on soaking cylindrical type Poly nitroester.**

Water temp. °C	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	Residual solvent content %
30	6	11.70	0.97	0.35
40	6	11.50	0.90	0.37
50	6	11.51	0.91	0.30
60	6	11.30	0.87	0.33
70	6	11.20	0.92	0.36

Table (7)

The effect of time on soaking cylindrical type Poly nitroester at 70°C.

Time ( hrs)	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	Residual solvent content %
2	6	7.65	0.81	0.35
4	6	7.70	0.87	0.40
6	6	7.61	0.90	0.32

Table (8)

The results of treatment cylindrical type Poly nitroester with 1.0 % (Ce) solution.

Time ( hrs)	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	(Ce) content %	Residual solvent content %
1.0	7	7.21	0.92	0.30	0.38
1.5	7	7.01	0.87	0.34	0.41
2.0	8	6.73	0.91	0.38	0.31

Table (9)

The results of treatment flake type Poly nitroester with 1.0 % (Ce) solution.

Time ( hrs)	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	(Ce) content %	Residual solvent content %
1.0	8	7.32	0.80	0.52	0.38
1.5	8	7.01	0.83	0.60	0.41
2.0	8	6.90	0.91	0.65	0.31

Table (10)

The results of treatment tubular type Poly nitroester with 1.0 % (Ce) solution.

Time ( hrs)	H.T (100 °C) Appearance of brown fumes (days)	B.J (132 °C) ml NO/ 5g nitroester	Moisture content %	(Ce) content %	Residual solvent content %
1.0	7	8.31	0.96	0.31	0.42
1.5	7	7.93	0.89	0.35	0.41
2.0	7	7.93	0.89	0.35	0.41

## Conclusion

As it has been mentioned in the results and discussion, there is an improvement in the stability results for all type using all the indicated treating methods.

However ,soaking method gave to some extent, an improvement in the stability results, this improvement was obtained as a results of the extraction of the harmful products from inside the nitro ester ,but the problem is that, the content of stabilizer in the powder is still less than the required percentage. This method can be used as a pretreatment method for other treating processes with (Ce) solutions.

Treating the unstable nitro ester with (Ce) solution gave the required stability results at all the treated types

We can optimize the conditions of treatment using (Ce) solution by setting the temperature at 70 °C and the flow rate (80-85) cm<sup>3</sup>/sec for two hours.

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