

N,N,N',N'-tetraacetyletylenediamine (TAED) as an Activator for Persodiums, in Modern Compositions of Detergents and Disinfectants

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The synthesis of N,N,N',N'-tetraacetyletylenediamine (TAED) in two steps was approached, using as a basic raw material ethylenediamine, this one being acetylated in the first step with acetic acid to give N,N'-diacetyletylenediamine (DAED), DAED being acetylated afterward with acetic anhydride up to TAED; both steps of the process are accomplished in a xylene medium. The purification of the raw product is made from a mixture of acetic acid and ethanol, giving TAED with a purity that allows it to be used in detergent and disinfectant mixtures. The activation capacity of the peroxidic compounds was tested using sodium percarbonate, as a single compound or in a mixture with TAED, on several bacteria.

Keywords: N,N,N',N'-tetraacetyletylenediamine, bleaching agent, peroxide activator, per-acid precursor, additive for detergents, disinfection

N,N,N',N'-tetraacetyletylenediamine (TAED) is an ecologic and extremely efficient activator for the persodiums (perborates, alkaline percarbonates etc.) that are part of the composition of the modern formulii for detergents, with the purpose of washing away as efficiently as possible the stained and the dirt agents, even at low temperatures, having at the same time remarkable disinfectant properties, without affecting cloth, colors or attacking the skin.

Characteristic for TAED is the high degree of purity where we can also get the high melting point, that ensures appropriate processing properties. Having a theoretical content of active oxygene of 140mg/g, it is capable of achieving a capacity of utilization superior compared to the similar products. The quite acetic smell and the acid pH are generated by the traces of acetic acid resulted after the synthesis process and that adheres to the TAED crystals.

The whitening on base of active oxygene generally represents a chemical process that takes place in at least two partial stages. During the first stage, the perhydrolysi, TAED reactions with the hydrogen peroxide resulted through solubilisation of the percarbonate. After the reaction two molecules of peracetic acid and DAED (diacetyletylenediamine) are generated, which are easily biodegradable compounds and without toxicity. The reaction takes place for a few minutes in the field of pH 10-11, being practically independent of the temperature.

The second step is the formation of active oxygene and the real process of whitening. Its mechanism, where the peracetic acid reacts with the chromophore systems of the dirt (stains) is not fully solved. The formation of active oxygene, meaning the transfer of a peroxidic oxygen from the peracid and after that the whitening process are influenced by the nature of the secondary batch as well by the value of the pH. On one hand, the atomic oxygene functions as a whitening agent, on the other hand the peracetic acid or its sodiums salt may act in the same direction. The real whitening reaction is a reaction of I

degree in relation with the oxidation agent and depends in great measure on the temperature in the field 20-50°C. Another crucial factor for the process of whitening is the access of the peracetic acid at the surface of the dirty fibre. The action mechanism of the activator is based on the formation of active oxygene according to the reactions in figure 1.

Each gram of TAED releases 0,67 g peracetic acid (or 0,14 active oxygene). According to the reaction stoichiometry, the relation between TAED and the perborate tetrahydrate should be of 1:1,35 or 1:0,9 in case of using perborate monohydrate. Still, in practice we use a little excess of persodiums in order to compensate their possible losses of activity because of the deposition or the decomposition under the influence of certain enzymes. In case of using the percarbonate, quite less stable than the perborate, its concentration in formulations must reach 10-15%. Concentrations of TAED less than 50 mg/L washing liquid will not produce an appreciable whitening activity, but an increase of the dose to 500 mg/L is associated to a constant increase of the degree of whitening.

Concerning the hygiene and decontaminant capacity imposed to modern detergents, even at temperatures under 40°C, where the activity of the hydrogen peroxide is not very good, especially for short washing cycles, the efficiency of decontamination can be substantially improved using additions of TAED, realizing at the same time a considerable enlargement of the antimicrobial action spectrum. This way, the systems containing TAED and persodiums are used in great proportion as disinfectant agents with powerful antimicrobial action.

Supplementary to the germicid action, these hygiene systems can totally remove the smells that adhere to clothes, as well as the smells of culinary products or of tobacco. Here as well we can see a lifting, a special accent of the activity by adding TAED in the combinations containing persodiums. This property is especially useful in the detergent perfumed formulas.

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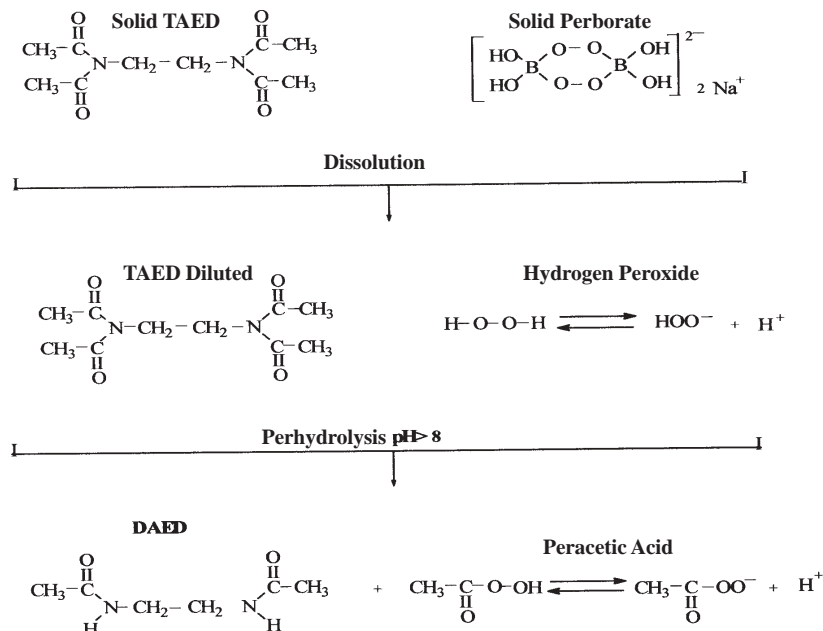


Fig. 1. Mecanism of TAED for sodium percarbonates

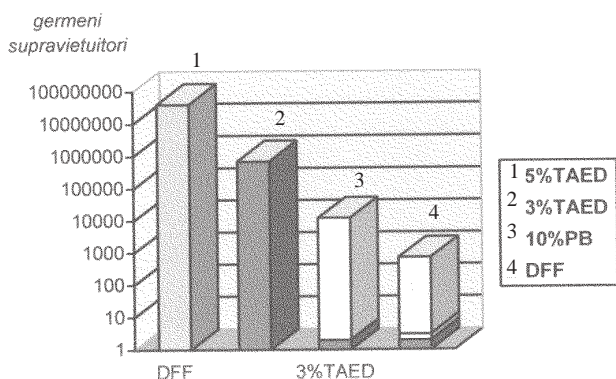


Fig. 2. Sterilizant effect of C. albicans germs

An eloquent example of synergy of the biocid activity by TAED is the action of the disinfectant systems on cell of *Candida albicans*. This one is proven to be greatly resistant at disinfectants with active oxygen base. Its proliferation is hardly managed by the detergents in the absence of disinfecting systems. Even at 40°C the addition of only perborate does not lead to the wanted effects. But, by adding in the composition a dose of 3-5% TAED, even at temperatures under 40°C, we can obtain a significant reduction of the content of germs, as we can notice in figure 2, where: DFF = detergents without phosphate compounds, 10PB detergent composition containing 10% monohydrate perborate, 3% TED = detergent composition containing 3% TAED, 5% TAED = detergent composition containing 5% TAED.

According to the literature in the field, TAED is obtained in the majority of the procedures during a two stages process, from the reaction between the etylenedyamine and the acetic anhydride.

During the first stage of the process, the etylenedyamine is diacetylated at the diacetyletylenedyamine (DAED) with the help of various acetylation agents: acetic acid, acetic anhydride, cetene. During the second stage, DAED together with the acetic anhydride are converted at TAED. Through reusing all the resulted secondary products, the procedure ensures an integrated and total protection of the environmental production, and as well a quality constantly raised of the product, of about 99%. The process

permits a continuous stage development, in the context of a high degree of automatization of the installation.

As agents of acetylation corresponding to the first stage, the literature of the field describes a series of compounds as: the acetic acid, the acetic anhydride, the cetene etc. The most used of them is the acetic acid, because of the convenient price and the fact that the secondary product resulted from the acetylation product is water, non-toxic and easily removable from the reaction mass.

In case of the second stage, the acetylation acid most used is the acetic anhydride, this one being generally used in great excess in relation with the necessary stoichiometric quantity. But in practice the utilization of acetic anhydride is limited, because it is included in the list of drugs precursors.

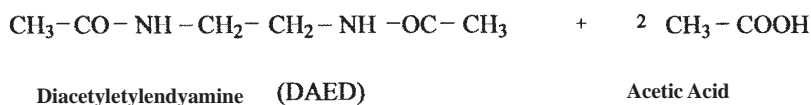
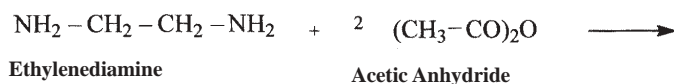
TAED raw resulted during the second stage presents as a pulverulent product, with a yellow-brown color and accentuated tendency of hydrolysis. But the utilizations of the final product TAED impose severe quality parameters, referring to purity and color. That is why the synthesis of TAED must be completed with operations for its purifying.

TAED is usually used in formulas of detergents or disinfectants in solid form, together with peroxide derivates and alkaline compounds. Their presence, together with the atmosphere humidity, diminish the stocking duration of the final product. That is why we chose to protect the TAED granules by covering with pelliculogen products and/or organic acids in solid state.

After having done the experiments, there was elaborated a procedure of obtaining purified TAED, ready to be used in detergent and disinfectant compositions. The elaborated procedure is made of three distinct stages, meaning the synthesis of the intermediary N,N-diacetyletylenedyamine (DAED), the synthesis of N,N,N',N'-tetraacetyletylenedyamine (TAED), the purifying and stabilization of N,N,N',N'-tetraacetyletylenedyamine (TAED), according to figure 3.

As well, a testing was made for the capacity of TAED as an activator of the peroxide compounds, made through the point of view of their microbiocid activity on a series of microbial cultures, alone and in combination with TAED. The results of the biological activity tests, made on a series of microbial steams, using TAED only and mixtures of TAED and a series of persodiums (Tetrahydrate sodium

Step I:



Step II:

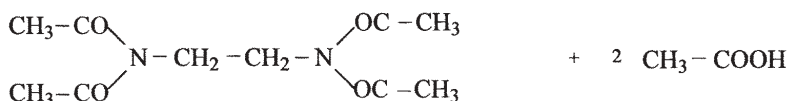
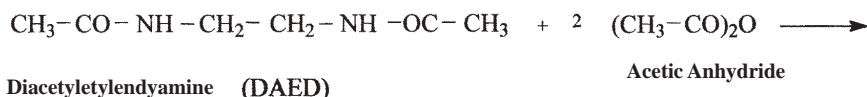


Fig. 3. Main reactions for achievement of TAED

perborate, sodium percarbonate) as well the object of the present article.

Experimental part

Stages of the researches made

The synthesis of N,N'-diacetyletylenediamine (DAED) is based on the reactions between the ethylenediamine and the acetic acid. (fig. 4).

The relation between the reactants is stoichiometric. The reaction takes place during two stages. First is, the neutralizing of the ethylenediamine with acid, forming a salt, the diacetate of the ethylenediamine. The reaction of neutralization is exothermic. During the second stage there is the amidation, though the elimination of 2 water molecules from the diacetate. The reaction is endothermic and needs heating. Being a reversible reaction, for the favorable movement of the equilibrium, the water must be eliminated from the system and it has been chosen the variant of its removing under the form of heterogeneous azeotrope, using xylene as a solvent. The water is

separated from the xylene, and the xylene is introduced again in the reactor. At first, there were used as solvents the xylene and the *n*-butyl acetate. Advantages and disadvantages have been quantified, related to the use of these solvents, together with the necessity of using a unique solvent during the two synthesis stages. The final option is for using xylene as a solvent.

Synthesis N,N,N',N'-tetraacetyletylenediamine (TAED) is based on the reactions presented in figure 5.

Initially, the study of acetylation was made in two variants: with high excess of acetic anhydride, this one being also a reactant and a solvent, and with little excess of acetic anhydride and with xylene as a solvent. Analyzing the advantages and the disadvantages of the two methods, an option was made for the second variant, using the xylene as a solvent, just like in the first stage of synthesis.

So, the synthesis of TAED was made by dosing (dropping) the acetic anhydride over the solution of DAED in the xylene, at the ebb temperature. The relation between

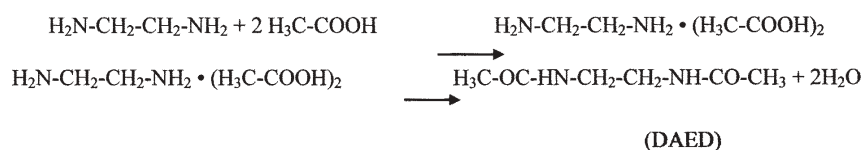


Fig. 4. N, N'-diacetyletylenediamine synthesis

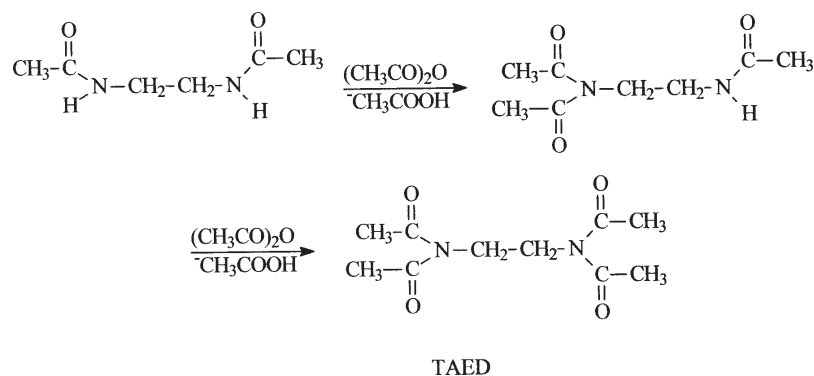


Fig. 5. N, N, N', N'-tetraacetyletylenediamine synthesis

xylene: DAED was of 1,3:1 (weight). The excess of acetic anhydride compared to the stoichiometric necessary is relatively low, compared to the former variant. The reaction takes place at the temperature of 130-150°C, from the reaction resulting acetic acid. The acetylation being a reversible reaction, the movement of the reaction equilibrium is favored by an excess of acetic anhydride and respectively by the removal from the system of the formed acetic acid. This is realized through a system of adjustment that permits the separation of the acetic acid under the form of azeotrope with the xylene, from the acetic anhydride. The azeotrope is separated in the collector basin for distillation, and the acetic anhydride comes back to the basin for reaction. The acetic azeotrope xylene is being recirculated in the process, being used in the first stage, of synthesis of DAED. So we distinguish a time of dosing (by dropping) the acetic anhydride, while the ebb distributor is being fixed on the total ebb regimen. The ebb distributor is then adjusted so as to maintain the temperature at the head of the column between $19 \pm 1^\circ\text{C}$. It is registered the time of reaction when the distillate formed mainly by acetic acid with xylene (azeotrope) is collected. After the ending of the reaction, the product obtained is being crystallized at cooling, is being filtered and is being washed on the filter with acetic acid.

The pat resulted after washing is passed to the next stage, of purification and stabilization of TAED. The filtrate and the solvent resulted from washing the pat will be reused for the next groups.

Purification and stabilization N,N,N',N'-tetraacetylenediamine

From the synthesis results TAED impurified with compounds brown in color. The utilizations of the product in the component of some detergent formulas with superior characteristics and in hygiene/disinfectant compositions need severe quality requests concerning the absence of the coloured impurities. By simple washing with various mixtures of solvents, the proper decolorization of TAED was not succeeded. Recrystallization operations from mixture of solvents in the presence of decolorizing carbon was necessary.

The crystals of TAED resulted after the purification and drying can be used as such. But in the compositions of detergents and respectively disinfection, TAED is used with percarbonates, perborates and other alkaline products. These ones, together with the humidity from the ambient air, initiate a slow degradation of TAED, so diminishing the decolorizing and disinfection capacity of the composition. That is why it is usually used the protection of the TAED crystals by covering them with pelliculogen substances, organic acids or a mixture of them. After the experiments concerning the establishing of an optimal method of protecting the TAED crystals, in order to ensure an effective protection as well simple operations, with minimal material and energy costs, it has been chosen the covering of the crystals with citric acid. This is being realized after washing the TAED pat on the filter with an alcoholic solution of citric acid. By drying the alcohol is removed and the citric acid remains on the TAED crystals.

The reactants used

The raw materials that are on the base of the synthesis, the purification and the stabilization of TAED are: *etylenediamine* (Etylenediamine p.s. made by Merck Schuchardt OHG Germany, of purity (according to GC) > 99% and water content < 1%), acetic acid (glacial acetic

acid produced by S.C. Chimopar s.a. Bucharest, with a min. content 96% and remaining after vaporization max. 0,002%), xylene (xylene p.a. produced by S.C. Chimopar S.A. Bucharest, formed of a mixture of isomers o-,m-,p-, having a distillation interval of 138-147°C min. 95% vol.), acetic anhydride (Acetic anhydride p.s. produced by Merck Germany, with content of active substance (according to the morpholine method min. 97,0%, etylic alcohol (Etylic alcohol p.a. produced by S.C. Chimopar S.A. Bucharest with a content of (C₂H₅OH), min. 96 % vol. and metanol (G.C.), max. 0,1 %) and decolorizing carbon produced by E. Merck AG Germany.

Description of the installation of synthesis of N,N,N',N'-tetraacetylenediamine (TAED)

The installation for the synthesis of N,N,N',N'-tetraacetylenediamine (TAED) is formed of a glass balloon with 4 necks, with dropping funnel, thermometer, system of electric stirring and distillation column filled with glass rings. The distillation column is coupled at the superior part with an ebb distributor, a condenser, a cooler and a collecting basin for distillation. The heating of the installation is made with a system of electric heating, with thermostat. The filtration of the product is made on a filter funnel type Büchner, with a collector basin for filtration, connected to a vacuum pump. The vacuum pump is protected by a trap for catching the steam. The washing of the TAED crystals is made with the same installation.

Results and discussions

On the product that we got this way and purified, a series of physical, chemical and biological determinations have been made: DSC, HPLC and testing the biocid activity.

The analysis of the final purified product TAED

TAED resulted after the stage of purification and drying was analysed using the technique analysis DSC and the analysis HPLC.

The DSC method

Experimental conditions: weight of the evidence 1-3mg weighted with an accuracy of $\pm 0,01\text{mg}$,

Atmosphere: N₂ at 50 cm³/min, initial temperature 80°C, final temperature 200°C. the evidence is introduced in a basin hermetically locked and weighed. The basin is then introduced in the cell DSC. Starting from 70°C under the nominal melting point the evidence is thermally programmed by its melting, whereas the thermal curve is registered in the memory of the computer. The evidence is programmed under the melting point to ensure the detection of the melting endotherm top. The low relation of programming (< 1°C/min) and the evidences of low weight (< 3mg) are used to ensure the equilibrium. Once the experiments finish the data are analysed and the results are printed using the Purity Program 1090.

Expressing the results. The determination of purity is made by the van't Hoff, equation, as follows:

$$T_s = T_0 - \frac{R \cdot T_0^2 \cdot \chi}{\Delta H} \cdot \frac{1}{F} \quad (1)$$

where:

- T - temperature of the evidence, °K;
- T_0 - melting point of the pure evidence, °K;
- R - gas constant (8.314 J/molK);
- χ - fractia molar fraction of impurities;
- ΔH - melting heat, J/mol;
- F - total fraction of the melted evidence at T_s .

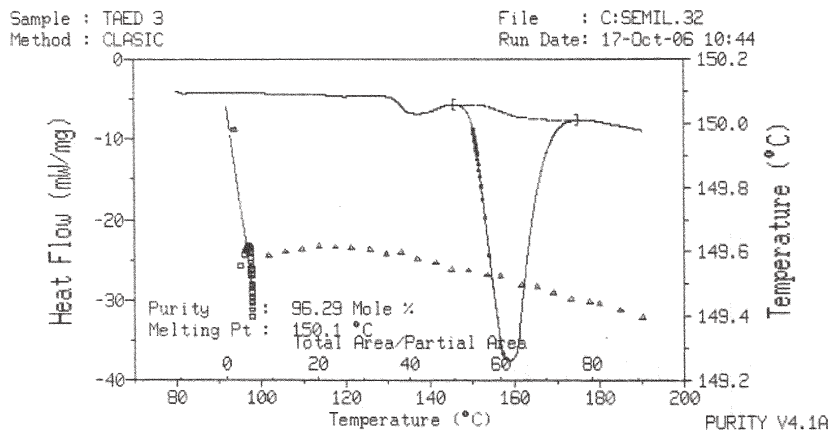


Fig. 6. Result of DSC analysis for a TAED sample

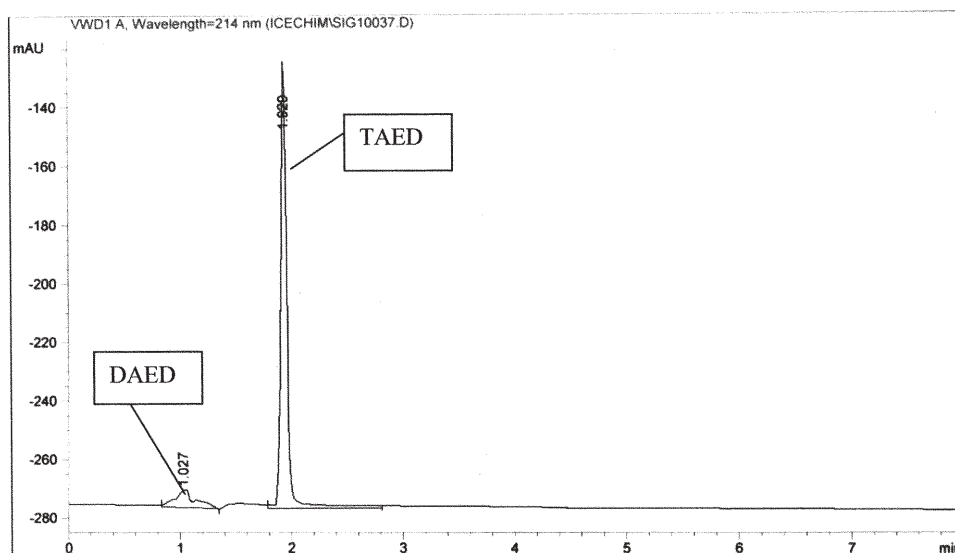


Fig. 7. HPLC chromatography for a TAED sample

The HPLC method

The evidence of TAED has been analysed, using a mixture of water solution and acetonitril, the acidification at a pH of 4 being made with fosforic acid. The relation water/acetonitril may vary from 50:50 to 50:35 considering the performance of the column and the nature of the interferent possibilities of the extracted compounds together with the TAED of the etyl acetate. Type of apparatus: Chromatographe for liquids Agilent Sistem 1100 HPLC.

Operating conditions HPLC. Column: ZORBAX Eclipse XDB-C18, 4.6 x 150mm, 5 μ ; mobile phase: 50% w/w -A (Acetonitril) + 50% w/w -B (distilled water); flow speed mobile phase: 1mL/min; Detector: VWD, λ =214nm, peakwidth (Response time): >0.1min(2s); injection volume: 20 μ L. The analysis of the TAED evidence has been made in relation with a standard of TAED, of known purity (98.55%), injecting 20 μ L as proof, respectively 20 μ L standard TAED solution, and the surface of the TAED peaks was calculated with the help of the calculator or of the integrator.

Obtained results: the result of the chromatographic analysis is presented in figura 6. This one underlines a purity of 96.85% of the TAED resulted after the purification stage, the major impurity being in the intermediary product DAED.

Biological activity tests

For the biological activity tests we used the following stems: Escherichia coli CIP54 127 (1) (ATCC 10 536),

Pseudomonas aeruginosa CIP A 22 (1), Staphylococcus aureus Oxford CIP 53 154 (1) (ATCC 9 144), Bacillus subtilis, in spored and vegetative form. Conditions of doing the biocid activity tests. The bacterian printed stems have been cultivated in peptonate liquid medium, static culture in tubes of 16/160mm, taking into account the following parameters: incubation temperature 37°C, cultivation time 24 h, no stirring, no air. At the end of the cultivation from every bacterian stem have been made smears (Gram coloration) that have been examined at the microscope in order to assess the bacterian purity and the fungic sterility.

The pure cultures have been used to test the bactericid activity of the following substances: sodium percarbonate, product p.a.; TAED (from 3 different groups); mixture TAED + sodium percarbonate (2:3), at dilutions 1/1, 1/2, 1/4 and 1/8, after 5 and 10 minutes of contact (culture + disinfectant). The antimicrobial effect has been tested with the method of the binary dilutions in aqueous medium of culture. From each dilution after 5 and 10 min of contact seedings have been made with ansa in Petri box with nutritive agar. The plates have been incubated for 48 h being examined at 24 and 48 h to assess the bacterian raising. The assessment of the development of the bacterin cultures was made taking into account the abundant raising of the culture on the seeding line, the low raising of the culture in rare colonies form and the absence of the culture raising. The obtained results are synthetically presented in tables 1 and 2. We add that anaerob microorganisms are by definition sensitive at the action of the oxidant substances.

Table 1
THE RESULTS OF THE TESTS OF BIOLOGICAL ACTIVITY OF AN AQUEOUS SOLUTION CONTAINING TAED 2%

No	Bacterian Strain	Incubation 24 h								Incubation 48 h							
		Contact Time 5 min				Contact Time 10 min				Contact Time 5 min				Contact Time 10 min			
		1/1	1/2	1/4	1/8	1/1	1/2	1/4	1/8	1/1	1/2	1/4	1/8	1/1	1/2	1/4	1/8
1	E. coli*	-	±	±	+	+	+	+	+	-	±	±	+	+	+	+	+
2	S. aureus*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3	Ps. aeruginosa*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4	B. subtilis*	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Legend: + Abundant Raising (culture) on line of seeding; ± Low Raising (culture) in form of rare colonies; - Lack of raising of the culture; Culture of 24 h

Table 2
THE RESULTS OF THE TESTS OF BIOLOGICAL ACTIVITY OF AN AQUEOUS SOLUTION CONTAINING TAED 2% + PERCARBONATE 3%

No	Bacterian Strain	Incubation 24 h								Incubation 48 h							
		Contact Time 5 min				Contact Time 10 min				Contact Time 5 min				Contact Time 10 min			
		1/1	1/2	1/4	1/8	1/1	1/2	1/4	1/8	1/1	1/2	1/4	1/8	1/1	1/2	1/4	1/8
1	E. coli*	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	S. aureus*	-	-	-	-	-	-	-	-	-	-	-	±	-	-	-	±
3	Ps. aeruginosa*	-	-	-	±	-	-	-	±	-	-	±	±	-	-	±	±
4	B. subtilis*	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Legend: + Abundant Raising (culture) on line of seeding; ± Low Raising (culture) in form of rare colonies; - Lack of raising of the culture; Culture of 24 h

Conclusions

There were studied the synthesis, the purification and the stabilization of N,N,N,N'-tetraacetylenediamine (TAED), for using in modern composition of detergents with superior capacity of whitening and disinfection.

The synthesized products were analytically characterized using the DCS and HPLC methods.

The antibacterial activity of the mixture of TAED and sodium percarbonate was tested, compared to the sodium percarbonate single, using 4 bacterian representative stems.

We notice an advanced inhibition of the raising of the bacterian cultures when using TAED, together with the sodium percarbonate, compared to the sodium percarbonate single.

The tested product has real microbicid properties, on aerobic and anaerobic bacteria.

The antibacterial action is obvious from the time of contact of 5 min, on all the tested species.

We consider that the product synthesised and tested by us can be used in modern compositions of detergents with high capacity of whitening and disinfection.

The product TAED + sodium percarbonate fulfil the conditions to be proposed for certification as decontaminant and/or disinfectant from the group of oxidants, according to the valid laws.

References

- *** Kirk & Othmer, Encyclopedia of Chemical Technology, Fourth edition, Ed. Wiley & Sons, London, UK
- HIMMIRICH, J., SCHULER, W., TAED – A versatile and efficient ingredient of modern cleansing products - Ed. Wiley & Sons, London, UK, 2003
- *** Clariant Annual Report 2004
- *** Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien (AISE) -Environmental Dossier on professional laundry - October 2002
- *** Human & Environmental Risk Assessment (HERA) on ingredients of European household cleaning products - Tetraacetylenediamine (TAED) (CAS 10543-57-4) - December 2002
- STEPAN, E., SERBAN,S., BURGHELEA, V., DINCA, V., Brevet RO 112612
- TOEPFER, H.J., Next-generation decon – NBC International, Summer, 2007

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