



The Ranking of Explosives by Use of Material Indices as Proposed in the Temclev-Ex Method^{*)}

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Abstract: The parametric system Temclev-Ex of fire and explosion hazard evaluation for devices and enterprises dealing with condensed explosives is presented. A brief description of the original Temclev method of evaluation and classification of the process hazard in chemical industry is given. The methodics of definition and estimation of the parametric indices characterising hazard level ensuing from constitutive properties of the reactive material is described. An exemplary evaluation of material indices for several explosives is made.

Keywords: process safety, material hazard indices, hazard evaluation

Introduction

Upon the growing area of commercial application of explosives there arises a significant demand for reliable methods of minimization of environmental and labor hazard connected with application of explosive materials. The presented paper outlines a parametric method Temclev-Ex designated for estimation of

^{*)} This work was supported by the State Committee for Scientific Research as a part of the project T09B 06325 “Adaptation of Temclev system to fire and detonation hazard assessment in manufacturing of explosives”.

the hazard level connected with production and exploitation of explosives and pyrotechnics. The Temclev-Ex method arises from Temclev system (Technology & Media Classification and Evaluation System) devoted to identification, evaluation and classification the process hazards in chemical industry that was developed at the Institute of Industrial Organic Chemistry in 1996-2000 [1-5].

In the paper base features of the Temclev-Ex system are presented. A particular attention is paid to methodic of choice, definition and estimation of parameters that are to represent hazard level connected with material properties of an explosive, like sensitivity to explosion initiation, the scale of potential range of damage, environment and health risk level etc. An exemplary evaluation of material indices for several condensed explosives is added.

An outline of Temclev methodology

The issue of Temclev method consists in parameterization of the hazard concerned with processing reactive materials. The plant, warehouse or other enterprise in which a hazardous material is employed is divided into the “process units”. Then a set of parameters characterising the selected unit is adjusted. The parametric characterization consist of three main groups of parameters: (1) parameters describing material (constitutive) properties of dangerous medium (e.g. explosive) that is present in the considered sub-system; (2) parameters characterising spatial and material features of the system and of the dangerous substance being processed (dimensions, volume, concentrations, technological aspects like the range of temperatures, exposition to uncontrolled activation impulses, etc.) and (3) characteristics of organization structure and safety procedures in which production or exploitation of the explosive is performed.

To each of the parameters being appraised a numerical value is assigned. Then, respectively to the prescribed rules final value of the resultant hazard index is evaluated. The method is of a comparative nature, i.e. considered installations, arrangements etc. are appraised along the same method. A part of the method is the risk scale corresponding to magnitude of hazard index. Then the hazard index for the newly analyzed unit is referred to the scale and, the hazard level for investigated arrangement is estimated. In this way, different objects concerned with production and exploitation of dangerous substances (explosives) can be compared.

The mathematical formula employed in Temclev approach for evaluation of the hazard level is as follow:

$$\mathbf{ZP} = [(\mathbf{W} + \mathbf{P}) \times \mathbf{S}] \times (\mathbf{T} / \mathbf{T}_{\mathbf{ZAB}}) \quad (1)$$

where **P** - fire index, **W** - explosion index, **T** - technological index,
S - specific material properties index, **T_{ZAB}** - protection index.

The indexes **W**, **P** and **S** are to describe constitutive properties of the dangerous medium (combustible substances, explosive atmospheres, oxidizing agents, etc.) that is present in the appraised process unit. **T** represents magnitude of the exposure concerned with particulars of technology in which the dangerous medium is processed. Index **T_{ZAB}** represents resultant magnitude of protective measures undertaken to diminish the imminence.

The material properties of a dangerous medium are comprised in two groups of fire index **P** and explosion index **W**. They accounts of the heat of combustion, self-ignition temperature (gases), flash point (liquids), ignition temperature of volatile thermal decomposition products (for dusts, powders or solids granular form), minimum ignition energy and a range of explosion (UEL-LEL, expressed in v/v %) of given gas or vapor. For dust-air mixtures only the lower explosion limits (LEL, expressed in g/m³) is used.

The sum of indexes **P** and **W** is enlarged by a value of specific material index **S** that take into account thermal stability of substances (**S₁**), their reactivity (**S₂**) and toxicity (**S₃**). It represents the influence of special properties of material that increase the fire-explosion hazard level and troubles that can arise in break-down fighting.

The technological index **T** takes into account several aspects of the processes that occur in the considered unit. It is evaluated as the sum of four groups of parameters:

- parameters characterizing general features of a process (operation) – **TO**;
- characteristics of physical processes occurring in the unit – **TF**;
- characteristics of chemical processes – **TP**;
- specific hazards characteristics – **TS**.

The protective measures which are embedded into index **T_{ZAB}** which may be of technical, technological and organizational matter, they are analyzed in four thematic groups:

- monitoring emergency states – **KS**;
- failure's preventive measures – **ZA**;
- emergency systems and control – **SA**;
- organization and safety management – **DO**.

More detailed characteristics of Temclev system can be found in [1-5].

On the base of results obtained with use of Temclev method an equation describing a hazard level of a process unit in which explosive is processed or manufactured has been proposed as follow:

$$\mathbf{ZP}_{\text{Ex}} = [(\mathbf{A}_{\text{Rw}} + \mathbf{B}_{\text{Rz}}) \times \mathbf{S}_{\text{Ex}}] \times [\mathbf{T}/\mathbf{T}_{\text{ZAB}}] \quad (2)$$

Here \mathbf{A}_{Rw} and \mathbf{B}_{Rz} represent material characteristics of explosive while \mathbf{S}_{Ex} describes its special properties. \mathbf{T} and \mathbf{T}_{ZAB} have the same meaning as in formula (1). By evaluation of \mathbf{T} and \mathbf{T}_{ZAB} the particular aspects of technology and treatment of explosives are to be included.

Estimation of material indices in Temclev-Ex method

In the Temclev-Ex approach the base material properties of an explosive are expressed by indexes \mathbf{A}_{Rw} and \mathbf{B}_{Rz} . \mathbf{A} and \mathbf{B} are the non-dimensional notes which are related to \mathbf{R}_w and \mathbf{R}_z – parameters describing explosive properties according to the Polish legislation.

The index \mathbf{A}_{Rw} represents vulnerability of the material to explosion initiation. It is estimated upon temperature sensibility of the explosive, friction and shock sensitivity. The values of incoming parameters are obtained in an experimental way. The index \mathbf{B}_{Rz} is based on explosion force and it is estimated upon results of thermochemical evaluations.

\mathbf{S}_{Ex} refers to specific properties of explosive material.

\mathbf{R}_w - sensitivity index is estimated upon the base of tests results. Three parameters are accounted:

\mathbf{T}_p – thermal decomposition temperature in the range from + 373 K to + 673 K,

\mathbf{R}_U – impact sensitivity in the range from 1J to about of 50 J,

\mathbf{R}_T – friction sensitivity in the range from 0.1 N to about of 360 N.

Then \mathbf{R}_M - mechanical sensitivity index, is obtained from the relation

$$\mathbf{R}_M = 0.076 (\mathbf{R}_U \times \mathbf{R}_T)^{1/2} \quad (3)$$

while \mathbf{R}_{Temp} - thermal sensitivity index is evaluated as

$$\mathbf{R}_{\text{Temp}} = 39.02 \times \log (\mathbf{T}_p/373) \quad (4)$$

The final value of \mathbf{R}_w is evaluated from formula

$$\mathbf{R}_W = (\mathbf{R}_M \times \mathbf{R}_{Temp})^{1/2} \quad (5)$$

The second component in formula (2), i.e. index \mathbf{B}_{R_Z} should appraise potential upshots of uncontrolled explosion. As the physical measure of the ability of detonation (explosion) products to perform work the \mathbf{R}_Z parameter is introduced. The value of \mathbf{R}_Z is estimated from the formula

$$\mathbf{R}_Z = 4.71 \times 10^{-4} (Q_w \times V_g)^{1/2} \quad (6)$$

where Q_w – heat of explosion and V_g – volume of explosion products (gaseous).

The way in which index \mathbf{R}_Z is defined should foresee the possible scale of damages to develop under circumstances of an irregular explosion/detonation. In the case of uncontrolled explosion the full development of detonative regime is as usually not attained. Moreover subjection to the damage of devices, installations deposited at various distances from explosive charge should be taken into account. Then to complain these circumstances as a magnitude of possible wreckage scale the product of explosion energy (Q_w) and gaseous product volume (V_g) has been chosen as it is expressed in formula (6).

For typical explosives the range of variability of \mathbf{R}_W and \mathbf{R}_Z can be as follow

- $0 < \mathbf{R}_Z < 1.10$ - the bigger its value – the higher hazard level,
- $0 < \mathbf{R}_W < 10$ - the bigger its value – the material lower sensitive,
- \mathbf{R}_M - the bigger its value – the material is of lower sensitivity;
- \mathbf{R}_{Temp} - the bigger its value – the material lower sensitive.

With an aim to perform a comparative analysis of hazard level concerned with material properties of various explosives, the scale has been built, for values of \mathbf{A} and \mathbf{B} . The value of indexes \mathbf{A} and \mathbf{B} is assumed as ranging from 1 to 25.

Table 1. Notes for indexes **A** and **B** versus values of material indices **R_W** and **R_Z**

Range of R_W value	Note of A_{R_W}	Range of R_Z value	Note of B_{R_Z}
9-10	1	1.05-1.10	25
8-9	2	1.00-1.05	20
7-8	3	0.95-1.00	16
6-7	4	0.9-0.95	15
5-6	5	0.85-0.9	12
4-5	6	0.8-0.85	10
3.54	8	0.7-0.8	9
3-3.5	9	0.6-0.7	8
2.5-3	10	0.5-0.6	6
2-2.5	12	0.4-0.5	5
1.5-2	15	0.3-0.4	4
1-1.5	16	0.2-0.3	3
0.5-1	20	0.1-0.2	2
0-0.5	25	0-0.1	1

Specific material index S_{Ex} is obtained as a sum of factors representing specific properties of the hazardous material. After analysis five features concerned with explosive properties of the material have been chosen to be incorporated into S_{Ex} value.

Then, for evaluation of a digital value of a specific material properties index S_{Ex} the following equation has been proposed:

$$S_{Ex} = 1 + \sum(S_i/10) \text{ for } i = 1, 2, \dots, 5 \quad (7)$$

S_1 – note for explosives properties (so-called “from deflagration/fire to detonation” susceptibility);

S_2 – note for electric/electrostatic spark sensitivity;

S_3 – note for elaboration of explosive hazard;

S_4 – note for toxicity of explosive material for humans and environment;

S_5 – note for toxicity of combustion/detonation products explosives to humans and environment.

The index S_1 is introduced to describe influence of run-up characteristics of explosive transformation (bulk explosion, DDT susceptibility, detonation in the whole mass) upon character of possible damages. Magnitude of S_1 index is estimated accordingly to European ADR classes.

Table 2. Index S_1 – a note for evaluation of influence of character of explosive transformation

ADR class	Description of ADR divisions of class 1 / HE type	Assumed note
1.1	Substances and articles which have a mass explosion hazard (which affects almost the entire load virtually instantaneously)	10
1.5	Very insensitive substances which have a mass explosion hazard (for example brisance explosives type B or E)	5
1.2	Substances and articles which have a projection hazard but not a mass explosion hazard	3
1.3	Substances and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard	2
1.4 1.6	Substances and articles which present no significant hazard and extremely insensitive articles which do not have a mass explosion hazard	1

Table 3. Index S_2 – a note for sensitivity to initiation through static electrical discharge (PN-E-05205:1997)

Sensitivity [J]	Degree of sensitivity to initiation through discharge of static electricity	Note in system
$W_{zmin} \leq 10^{-6}$	Quite unusually sensitive explosive	5
$10^{-6} < W_{zmin} \leq 10^{-5}$	Very sensitive explosive	4
$10^{-5} < W_{zmin} \leq 10^{-4}$	Average sensitive explosive	3
$10^{-4} < W_{zmin} \leq 10^{-2}$	Hardly sensitive explosive	2
$10^{-2} < W_{zmin} \leq 1$	Very hardly sensitive explosive	1
$1 < W_{zmin}$	Practically insensitive	0

In case lack of data, to assume:

Sensitivity [J]	Note of sensitivity for CSE	Note in system
$W_{zmin} = 10^{-6}$	Initiation explosive	5
$W_{zmin} = 10^{-4}$	Pyrotechnic or propellant	3
$W_{zmin} = 10^{-3}$	Brisant explosive	2

On accidental sources of combustion/explosion initiation can be a discharge of electrostatic charge. In Temclev-Ex system the sensitivity of HE for static charge is comprised in special index S_2 . Base of note for index S_2 is minimal electrostatic ignition energy W_z . Susceptibility to electrostatic discharge of

the hazardous material is estimated in accordance to Polish governmental standards.

By predicting the hazard range of a considered explosive charge, an influence of the package properties, i.e. the properties of charge casing should be accounted. To incorporate an influence of the kind of package in which the explosive is put up the index S_3 has been introduced. Strong materials, which can hurt with shrapnel have in high level notes (of 4-5 points) while soft packages are appraised by 0-1 points.

Table 4. Index S_3 – a note of hazard level due to explosive disruption of HE charge shell

Kind of border, boxes	Note in system
Thick metal (≥ 1 mm)	5
Thin metal (< 1 mm), glass	3
Thick wood, thick and hard plastic (≥ 5 mm)	2
Thin wood, plywood, thin and hard plastic (< 5 mm)	1
Paper, foil, cardboard, fibber, polyurethane foam, etc.	0

By contact with atmosphere or surrounding devices the explosive, considered as a chemical medium, can a source of undesirable influence upon human or environment. Then, a hazard concerned with undesirable affectation of explosive should be also taken into account. In the Temclev-Ex approach toxicity of explosive materials is appraised along with classification of particular chemical substances as established by decree of the Polish Ministry of Health.

Table 5. Index S_4 – a note for toxicity of HE to humans and environment

Indication of particular risk on the base of MZ dated 2-09-2003 (Dz. U. Nr 171 poz. 1666 z 2003 r.)	Description and scale of hazard	Note in system
R26, R27, R28, R32, R35, R39, R50	Large hazard (T+, C)	5
R23, R24, R25, R29, R31, R34, R45, R46, R49, R48, R51, R54, R55, R56, R57	Medium hazard (T, C)	3
R20, R21, R22, R33, R36, R37, R38, R40, R41, R42, R43, R52, R53, R58, R59, R60, R61, R62, R63, R68	Hardly hazard (X _n , X _i)	1
Explosives with no R appointed	Practically no hazard	0

The toxicity of products (combustion or explosion) is a very important factor. Its influences upon possibility of explosives use in closed space (e.g. in mines). Also the rescue action can be hindered by presence of toxic combustion products.

There are several methods developed for examination of toxicity of detonation products. One of them is measurement of content of noxious substances by explosion of a charge of a given mass (e.g. 0.5 kg) in a closed chamber (e.g. of 10 m³ volume). Then, the composition of reaction products is analyzed with use of chromatography, to estimate concentration of unfavorable ingredients. Also in this approach, it is important to perform all investigations (for all considered explosives) in the same conditions. In various countries several differences can be noted, in measurement methods and values of acceptable concentration of particular substances (e.g. NO_x, CO) [13].

By testing of Temclev-Ex system an analysis has been performed of composition products of various explosives. Both composition by explosion in constant volume (i.e. in first stage of process) and at constant pressure (when explosion/detonation products expand to atmospheric pressure) were evaluated. In this approach no influence of surrounding atmosphere (reaction with oxygen, heat exchange to surroundings) was included. Therefore obtained values of concentrations of noxious substances are depending only on material properties (chemical composition) of investigated explosives.

Exemplary results of numerical analysis are presented in Table 6.

Table 6. Toxic substances content in exemplary condensed explosives

Explosive	Chemical formula	Conditions of explosion	NO _x + HCN + NH ₃ [ppm]	CO [ppm]	S ₅
2,4,6-Trinitrotoluene (TNT)	C ₇ H ₅ N ₃ O ₆	P = 0.101325	HCN: 3300	599 800	3
		V = const	NO _x : 27 HCN: 1630 NH ₃ : 9300	320 000	
Hexogene (RDX)	C ₃ H ₆ N ₆ O ₆	P = 0.101325	NO _x : 4500	245 000	2/3
		V = const	NO _x : 320 HCN: 920 NH ₃ : 11300	320 000	
PETN	C ₅ H ₈ N ₄ O ₁₂	P = 0.101325	NO _x : 7700	225 000	2
		V = const	NO _x : 1700 HCN: 110 NH ₃ : 2100	130 000	

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)	C ₆ H ₆ N ₆ O ₆	P = 0.101325	NH ₃ : 3	500 000	2/3
		V = const	NO _x : 0.4 HCN: 2400 NH ₃ : 3300	345 000	
Hexanitrostilbene (HNS)	C ₁₄ H ₆ N ₆ O ₁₂	P = 0.101325	HCN: 110700	666 500	3
		V = const	NO _x : 0.1 HCN: 10500 NH ₃ : 110	669 500	
Picrid acid	C ₆ H ₃ N ₃ O ₇	P = 0.101325	NO _x : 50	611 000	2/3
		V = const	NO _x : 5 HCN: 3300 NH ₃ : 2500	502 000	
Octogene	C ₄ H ₈ N ₈ O ₈	P = 0.101325	NO _x : 4400	245 000	2/3
		V = const	NO _x : 295 HCN: 900 NH ₃ : 12200	173 000	
Tetryl	C ₇ H ₅ N ₅ O ₈	P = 0.101325	NO _x : 163	550 000	2/3
		V = const	NO _x : 21 HCN: 4400 NH ₃ : 5000	440 000	

Upon results of quantitative analysis, an average way of estimation of toxic properties of explosives belonging to various kinds of explosives has been proposed.

Table 7. Index S₅ – Averaged note for toxicity of combustion decomposition/fire products explosives to humans

Kind of explosives	Toxicity products like:	Note in system
Secondary explosives	CO, NO _x ,	2
Propellants	SO _x , HX, HCN,	3
Pyrotechnics materials and initially materials	Polycyclic aromatic compounds, smokes which contain: Ba, Hg, Pb, P ₂ O ₅ , ect.	5
Other HE	Without toxicity of combustion decomposition/fire products explosives or are they but in small amount	0 / 1
Unfavorable conditions of atmospheric, shape of area, buildings, indoor, additional local difficulty for action rescue	Additional note	+ 2

Table 8. Individual sheet of HE parameters

Polish name		Pentryl	
English name		Pentaerythritol tetranitrate	
Synonyms		Tetraazotan pentaerytrytu, nitropenta, PETN	
Composition		-	
Chemical formula		$C_5H_8N_4O_{12}$	
Other datas		CAS Number: 78-11-5, brisant explosive	
Note	Base of note	Source of datas for note	Comment
A_{Rw}	12	R_{Wv} 2.05	According to PN-93/C-86010: WNU = 3,0 J According to PN-C-86019:1994; WNT = 60 N According to BN-76/6091-08; T: = 475 K
B_{Rz}	20	R_z 1.01	BN-80/6091-42 C_{wv} 5901kJ/kg, V_p 779.5 dm ³ /kg
S_1	10	Transport classification	In regulation of transport of dangerous good exist UN 0150 PENTAERYTHRITOL TETRANITRATE (PENTAERYTHRITOL TETRANITRATE; PENT), WETTED WITH NOT LESS THAN 25% WATER, BY MASS, OR PENTAERYTHRITOL TETRANITRATE (PENTAERYTHRITOL TETRANITRATE; PENT), DESENSITIZED WITH NOT LESS THAN 15% PHLEGMATIZER, BY MASS BUT IN SPECIAL PROVISIONS APPLICABLE TO CERTAIN ARTICLES OR SUBSTANCES UNDER Nr 266 WE CAN READ „ THIS SUBSTANCE, WHEN CONTAINING LESS ALCOHOL, WATER OR PHLEGMATIZER THAN SPECIFIED, SHALL NOT TO BE TRANSPORTED UNLESS SPECIFICALLY AUTHORIZED BY COMPETENT AUTHORITY ”
S_2	1	W_{Zmin} $6.2 * 10^{-1}$ J	
S_3	0		
S_4	1	R3	Under the act: Dziennik Ustaw, Attach. to: No 199, item 1948 dated 24 November 2003; "Wykaz substancji niebezpiecznych wraz z ich klasyfikacją i oznakowaniem".
S_5	2	W 2	Explosion conditions Concentration of main toxically, gas product of explosion [ppm] CO: 255000 NO _x : 7700 P = 1013.25 hPa CO: 130000 HCN: 110 V = const NO _x : 1700 NH ₃ : 2100
$(A_{Rw} + B_{Rz})$	S_{Ex}	Material index of explosives	The sheet made by:
32	2.4	76.8	Date

For practical use there is important to elaborate a set-up of all parameters necessary to appraise and evaluate a hazard level. A new pattern has been worked out of individual sheet of explosive characteristics that includes information needed for explosive classification with requirements of Temclev-Ex method. The sheet contains data from literature and experimental results. New pattern of sheet is shown in Table 8 (example – “Pentryt”).

Ranking of explosives in Temclev-Ex method

Estimation of material indices A_{Rw} , B_{Rz} and S_{Ex} enables to prepare an analysis of a given process unit in which dangerous material (explosive) is processed. The product of $[(A_{Rw} + B_{Rz}) \times S_{Ex}]$ forms a base to appraise the process unit (comp. equation (2)).

Upon the results of estimation of material indices an comparison of hazard level coming from constitutive properties of various explosives can be made. An exemplary the “Ranking list of explosives” as obtained in Temclev-Ex system is presented in Table 9.

Table 9. Ranking list of explosives (an example)

Name of substance	A_{Rw}	B_{Rz}	Sum $A+B$	S_1	S_2	S_3	S_4	S_5	Sum $S_i/10$	S_{Ex}	Material index of explosives
Nitroglycerine	15	16	31	10	2	0	3	2	1.7	2.7	83.7
Tetracene	20	10	30	10	1	0	3	3	1.7	2.7	81
Lead azide	20	3	23	10	5	0	5	5	2.5	3.5	80.5
Mercury fulminate	20	4	24	10	3	0	5	5	2.3	3.3	79.2
Pentaerythritol tetranitrate	12	20	32	10	1	0	1	2	1.4	2.4	76.8
Lead trinitrosorcinate	20	4	24	10	4	0	1	5	2	3	72
Hexogen (RDX)	9	16	25	10	2	0	1	2	1.5	2.5	62.5
Pentaerythritol tetranitrate desensitized	10	15	25	10	1	0	1	2	1.4	2.4	60

Nitroglycerine propellant	9	10	19	10	3	0	3	2	1.8	2.8	53.2
ANFO	5	15	20	10	2	0	1	2	1.5	2.5	50
Nitrocellulose 11%	10	9	19	10	3	0	0	2	1.5	2.5	47.5
Nitrocellulose propellant	10	12	22	2	3	0	3	2	1	2	44
Trinitrotoluene	4	10	14	10	2	0	3	3	1.8	2.8	39.2
Picric acid (TNF)	5	9	14	10	2	0	3	2	1.7	2.7	37.8
NTO	3	9	12	10	2	0	5	2	1.9	2.9	34.8
Black powder	3	4	7	10	2	0	0	5	1.7	2.7	18.9

The results presented in Table 9 concern properties of pure substances. Then, the value of index S_3 which refers to the potential damage that can be caused by disrupted shell, massive covering etc. of explosive charges is omitted, the value of S_3 is put to be equal of 0.

Practical employment of Temclev-Ex system

One of the very important parts of the system is a possibility to their effective use. As a part of the project is construction of necessary tools that will enable to perform the analysis along with the rules defined above.

One of the elements of the system is a manual “Temclev-Ex” in which all procedures of evaluation of indices A_{Rw} , B_{Rz} and S_{Ex} as well as T and Tz_{AB} are described.

Also, a numerical package is constructed by which all the process hazard analysis and reporting can be performed. The developed software is intended to carry out further investigations upon the system as well as for use by technical staff in industry units, to perform current analysis of the security of processes in which explosive materials are involved.

Conclusions

1. The parametric system Temclev-Ex intended for evaluation and classification of fire and explosion hazard connected with production and exploitation of condensed explosives has been presented.
2. The methods of evaluation of the material indexes A_{Rw} , B_{Rz} and S_{Ex} that represent hazard level resulting from physicochemical properties of explosive have been described.
3. Pattern of sheet comprising information about explosive which are needed for its evaluation and classification in Temclev-Ex system have been worked out.
4. Exemplary ranking of explosives as obtained by the Temclev-Ex system has been presented.
5. The role of numerical software in implementation of the described procedure has been outlined.

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