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Review / Przegląd

Natural and synthetic waxes in explosives – a review
Przegląd naturalnych i syntetycznych wosków stosowanych w materiałach wybuchowych

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Abstract: *The aim of the paper was to determine how many natural waxes are used in explosives and whether it is possible to make the waxes independent of natural sources. A review of natural and synthetic waxes used in explosives was made. The object of the review was literature not only closely related to explosives, but also other specialistic sources allowing for the identification of components used in materials called waxes. About 40 waxes have been identified that have been or are used in explosives in the world over the last 80 years. A mixture called a wax can therefore contain 2-5 different ingredients and practically none of the ingredients need to be a wax in the narrow sense. The rest of ingredients of the compositions called waxes are surfactants, emulsifiers, emulsion stabilizers, film-forming additives, etc. The composition and properties of about 20 of the most popular wax-containing explosives are presented. The results indicate that in next 10-20 years resignation from natural waxes is unlikely.*

Streszczenie: *Wykonano przegląd wosków naturalnych i syntetycznych używanych w materiałach i kompozycjach wybuchowych. Zidentyfikowano ok. 40-tu wosków które były lub są stosowane w materiałach wybuchowych na Świecie na przestrzeni ostatnich 80 lat. Ustalono, że w literaturze przedmiotu terminem „wosk" zwykle określa się topliwą nieenergetyczną mieszaninę na bazie wosków naturalnych lub syntetycznych. Mieszanina nazywana woskiem może więc zawierać 2-5 różnych składników i praktycznie żaden ze składników nie musi być woskiem w wąskim tego słowa znaczeniu. Pozostałe składniki kompozycji nazywanych woskami to środki powierzchniowo czynne, emulgatory, stabilizatory emulsji, dodatki filmotwórcze itp. Przybliżono skład oraz właściwości ok. 20-tu najpopularniejszych kompozycji wybuchowych zawierających woski. Analizowane kompozycje wybuchowe można elaborować techniką prasowania lub odlewania.*

Keywords: *explosives, explosive compositions, waxes, natural waxes, synthetic waxes, physical properties, energetic properties*
Słowa kluczowe: *materiały wybuchowe, kompozycje wybuchowe, woski, woski naturalne, woski syntetyczne, właściwości fizyczne, właściwości wybuchowe*

1. Introduction

Waxes are a broad group of chemical compounds that are defined by physical and functional properties rather than typically chemical properties. The group of waxes usually includes chemical compounds meeting criteria such as being solid at a minimum up to a temperature of about 40-50 °C, lipophilicity, hydrophobicity, plasticity at the temperature of use, and physical and chemical stability in the liquid phase [1]. Wax refers to both chemical compounds and their mixtures – having the properties listed above. These can be mixtures of compounds from one homologous series as well as compositions of compounds of different chemical nature. The first waxes used in technology (not only military) were of natural origin but, with the development of chemical technology, synthetic waxes were increasingly used. Synthetic waxes are understood to be not only artificially produced analogues of natural waxes, but also substances produced entirely synthetically and having no natural analogues. The division of waxes at a high level of generality is based on the criterion of their origin. Waxes are therefore divided into natural and synthetic. For natural waxes, two subgroups are traditionally separated:

(1) waxes obtained from crude oil, and
(2) waxes from sources other than crude oil.

The earliest wax used by man was probably beeswax used in ancient Egypt for candles, cosmetics, etc. [2]. It is assumed that the word wax comes from the Anglo-Saxon word *weax*, which meant *beeswax*. Accounts of the use of shellac in ancient India [3] for ornamental purposes and as a protective material for objects of great value date to a similar time. Despite the passage of several thousand years since the first documented human use of waxes, both beeswax and shellac are still used in technology and art. Thanks to developments in chemical analysis and chemical technology, at least several hundred waxes (most of them synthetic) are now known with properties that are closely tailored to consumer needs.

In military technology, waxes were used long before the introduction of weapons containing explosive material (EM). The beeswax mentioned was used in the process of making bows, then as a lubricant for muskets. The first use of wax to reduce the susceptibility of high explosives occurred around 1940 when it was used in a melt-cast hexogen/TNT (60/40) composition. A second example of the mass use of a wax desensitised explosive was the introduction of desensitized pentrite (pentaerythritol tetranitrate, PETN) by the Germans during the Second World War. Since then, the desensitization of explosives with waxes has become commonplace and practically continues to this day. For some modern pressed explosive compositions, waxes (natural and synthetic) have been displaced by synthetic fluorine rubbers such as Viton (DuPont), Dyneon (3M), etc.

Despite the rapid development of materials engineering and the chemical industry resulting in the development of excellent synthetic desensitization materials, the role of waxes in modern technology (including military technology) is still large. According to official data, wax consumption in the USA alone in 2016 was 140,000 Mg [4].

2. Overview of the properties of waxes used in explosive compositions

Coating the crystals of initiating and crushing explosives with natural and synthetic waxes is called desensitization. It aims to reduce the sensitivity of the explosive to a level that allows it to be handled safely during production, elaboration and use. Covering EM crystals with waxes reduces sensitivity by:

(1) physically separating the crystals with a layer of wax,
(2) absorbing and dissipating the heat generated when the crystals rub against each other,
(3) the eventual ignition of the composition leads to heat absorption by the endothermic melting process of the wax.

Due to the widespread use of Composition B (RDX/TNT 60/40) for military purposes, the role of waxes in its manufacture has been studied in detail. In addition to the above-mentioned factors affecting the reduction in sensitivity, it has also been noted for Composition B (and other TNT-containing compositions) that the wax fills the pores formed during TNT solidification which results in a reduction in gas bubbles forming so-called hot spots [5, 6].

When selecting the type of wax to modify an explosive composition, the following parameters should be taken into account:

(1) the solubility of the wax in the fusible components of the composition (e.g. TNT). The Hildebrand solubility parameter can be used to quantify the interactions occurring between the components.
(2) Wettability of a solid component (e.g. hexogen, RDX) by a wax or wax/energy fusible component composition (e.g. TNT).
(3) Wax melting point in relation to the energetic fusible component. This parameter affects the dispersion/dissolution efficiency and thermal stability of the composition. It is advantageous for the wax to have a higher melting point than the explosive to avoid evaporation.
(4) Chemical compatibility: the wax should not react with the ingredients or catalyse their decomposition.
(5) The viscosity of the wax at elaboration temperature should be lower than that of the other melt components or the viscosity of the emulsion should be lower than that of the least viscous component.
(6) A high specific heat (and melting heat) value is preferred so that even with a low content, the wax is able to absorb as much heat as possible.
(7) Mechanical properties should promote the reduction of sensitivity. The wax should therefore not be too brittle and crack, but also not too flexible as it will store energy that should be dissipated. For the wax to effectively desensitise the crystalline MW, it should be less brittle than it and have a slightly higher elasticity.
(8) The wax used in the explosive composition should have highly reproducible properties, be available and as low in price as possible.

Due to the strategic nature of the information on explosive compositions used in the armies of different countries, as a rule manufacturers and users very rarely provide the full physico-chemical specifications of explosives. The widespread access to knowledge prevailing in democratic countries has meant that it is more or less known what the main component of most even advanced explosives and compositions is. Despite this, manufacturers effectively protect information on key additives and modifiers. This group includes waxes. With a few exceptions, the literature usually does not indicate that wax is used in the composition and, if such information is given, it is rarely possible to find out what wax and in what quantity was used. A good example to illustrate this point is the D2 wax referred in many sources. It is relatively difficult to find out what its composition is and how (technology-wise) it is obtained. The composition of the said wax is given in Table 6 [5, 7].

An extensive review of the literature on the use of waxes in explosives and explosive compositions shows that about 40 different natural and synthetic waxes have been used at different times in different countries around the world. An important factor in the choice of wax for explosive compositions used for military purposes is the raw material base found in a particular country. For this reason, palm wax, for example, was and is used in equatorial countries and waxes extracted from bamboo leaves were used in Asian countries. A full list of waxes identified for use in military products is shown in Table 1. The waxes mentioned are rarely chemical individuals such as stearic acid; they are usually mixtures of compounds of natural or synthetic origin, and even in the case of synthetic compounds they are usually mixtures of compounds from the same homologous series. Also widely used for civilian purposes (including in the food industry), Carnauba wax is a mixture of aliphatic esters, 4- and ω-hydroxycinnamic acid esters and fatty series alcohols. Composed by natural selection in the palm tree (from the genus Copernicia waxwort), it has unique properties and this wax is considered one of the most durable in nature. In countries with access to oil deposits, so-called earth waxes were and still are popular, from which ceresin, ozocerite, paraffins, etc. are extracted. In countries with access to coal and lignite deposits, so-called Montana waxes are popular. Virtually every latitude uses the aforementioned beeswax.

The melting points of the waxes analysed range from 60 to 180 °C, with 70-80 °C being the most common range. The highest melting points are characteristic of the corresponding synthetic waxes, e.g. Chlorowax, polyethylene waxes and ethylene-vinyl acetate copolymers.

Table 1. Waxes used in service and experimental explosive compositions

Name of the wax	**Melting point** [°C]	**Reference**
Bamboo leaf wax	78-80	[8]
Bareco X404	86	[1]
Bareco X715	84	[1]
Castorwax NFM	86	[1]
Cerezine	61-72	[9]
Chlorez 700-SS	115	[1]
Chlorowax 57-58	60	[6]
Chlorowax 70-200	70	[6]
Esparto wax	68-78	[10]
Ethylene-vinyl acetate	70-180	[11]
Indramic 170C	84-86	[1]
Indramic 800	83-89	[1]
Stearic acid	69-71	[12]
Ouricury wax	81-84	[13]
Ozokerite	60-100	[14]
Paraflint C1	89	[15]
Paraflint A3	127	[15]
Paxwax 7517	88	[5]
Petrolite CP-7 (copolymer)	95	[1]
Petrolite Ultraflex	64	[1]
Petrowax 9508	90	[16]
Polywax 500 (homopolymer)	89	[6]
Polywax 600 (homopolymer)	92-94	[6]
Polywax 655 (homopolymer)	99.5	[6]
Reed wax 6884	70	[5]
Rosswax 561114	66	[1]
Rosswax 561204	70	[1]
Sugarcane wax	75-80	[17]
Sunoco 1290	67	[1]
Sunoco 8810	77	[1]
Candelilla wax	65-69	[1]
Wax of Knoxville 123	69	[1]
Western Mekon	89	[1]
Carnauba wax	83-86	[18]
Hemp fiber wax	74-81	[19]
Montana ALPCO 16 wax	81-85	[20]
Montana Hoechst S wax	84	[20]
Montana Hoechst KPS wax	82	[20]
Paraffin wax	38-54	[1]
Polyethylene AC629 wax	100.6-105.0	[21]
Polyethylene AC400 wax	105	[21]
Beeswax	68-70	[18]

3. Overview of explosive compositions containing waxes

Velicky [5] investigated in detail the effect of the wax content of the chloroparaffin group (Chlorowax) on the shock wave sensitivity of cast RDX/TNT/wax compositions (Table 2). The author noted that initially an increase in wax content results in a sensitisation of the composition. Once the wax content exceeds 4%, the sensitivity starts to decrease.

Table 2. Compositions tested to determine the effect of wax content on sensitivity to mechanical stimuli [6]

Ingredient	Content [%]			
RDX	60.0			
TNT	39.0	38.0	36.0	30.0
Chlorowax	1.0	2.0	4.0	10.0
Sensitivity	6.5	7.5	9.5	9.0

As part of the search for new solid waxes for TNT compositions, the effect of the addition of the compound on the peak temperature of the exothermic decomposition of the composition as determined by the DSC technique was investigated [5]. The test results are presented in Table 3. Compositions containing 25% of the additive were tested regardless of whether it dissolved in TNT completely or an emulsion was formed. It was noted that only triphenyl phosphate (TPP) increases the peak temperature value of TNT decomposition, making it promising for future applications.

Table 3. Study of the effect of waxes on the decomposition temperature of a wax/TNT mixture (25/75) [7]

Compound	Additive is soluble (R), insoluble (N) or emulsifiable (E)	Decomposition temperature [°C]
TNT (99.5%)	–	300
Kenamide E	E	250
Kenamide S180	N	281
Kenamide S221	N	265
Kenamide S	E	280
Triphenyl phosphate (TPP)	R	312
Aclyloid DM55	N	281
Unithox 550	N	270
Kraton D1101	N	244
Ethylene-vinyl acetate (AC-400)	N	285

Wilson [21] studied hexogen compositions with the synthetic polyethylene wax AC629 with the compositions shown in Table 4. The highest density of the pressed composition was obtained for the highest hexogen content, but the highest value of detonation velocity was recorded for the composition containing 7.7% wax, which does not have the highest density among the mouldings tested. The authors explain this phenomenon by obtaining the highest density relative to the theoretical density in a number of compositions tested.

Table 4. Physical and explosive properties of pressed RDX compositions – wax AC629 [21]

Composition	Density [g/cm^3]	Detonation velocity [km/s]
RDX/wax (95.2/4.8)	1.642	8.19
RDX/wax (92.3/7.7)	1.620	8.21
RDX/wax (88.4/11.6)	1.552	7.93
RDX/wax (87.5/12.5)	1.510	7.68
RDX/wax (86.5/13.5)	1.521	7.76

Table 5 provides an overview of explosive compositions containing waxes for which a quantitative composition has been established. Determining the qualitative composition was not always possible due to the strategic nature of this type of information. Available information on detonation parameters is presented for each composition. The simplest examples are two-component compositions containing a strong high explosive (hexogen, octogen, pentrite) and wax. Also popular are three-component compositions containing, apart from the high explosive and wax, the addition of aluminium powder (e.g. A-IX-2). In many cases of fusible compositions with aluminium, the wax acts as a modifier to prevent sedimentation of the components during solidification (AFX-644, TGAG-5). In the case of more contemporary compositions, it is possible to find information that, in addition to wax, advanced surfactants are used, e.g. Indramic-800 in the AFX-645 composition. In some compositions, compounds with plasticising properties (e.g. 2-ethylhexyl acrylate (EHA)) can be found, indicating that in some compositions the hardness of the wax, e.g. carnauba, is too high. Analysing table 5, it is easy to see that the literature only gives information on the type of wax used in some cases. Usually, the information is limited to the fact that wax is used.

Table 5. Multicomponent explosive compositions containing waxes

Designation	Composition	Density [g/cm^3]	Detonation velocity [km/s]	Reference
A-IX-1 or Comp A	RDX/wax (95/5)	1.65	7950	[22]
A-IX-2	RDX/Al/wax (73/23/4)	1.75	7330	[7]
A-3	RDX/Al/wax (64/30/6)	1.82	7420	[23]
AFX-644	TNT/NTO/Al/wax (30/40/20/10)	1.90	7312	[24]
AFX-645	TNT/NTO/Al/(Indramic-800/ganex-660) (32/48/12/8)	1.63	6830	[24]
Dentex	RDX/TNT/Al/Wax (48.5/33.5/18/1)	1.81	7780	[22, 25]
EDC-1	HMX/RDX/TNT/wax (70/4/25/1)	1.84	8330	[25]
H6	TNT/Al/RDX/$CaCl_2$/wax (29.5/21.0/44.0/0.5/5.0)	1.74	7300	[26, 31]
HBX-1	TNT/RDX/Al/wax (38/40/17/5)	1.72	7300	[5, 27]
HBX-3	RDX/TNT/Al/Wax/$CaCl_2$/additives (31.3/29/34.8/4.9/0.5)	1.85	7530	[22]
B-2	TNT/RDX/wax (39.5/59.5/1.0)	1.65	7800	[7]
Okfol	HMX/wax (95/5)	1.72	8300	[22]
TGAF-5	TNT/RDX/Al (40/40/20)	1.80	7600	[5]
TGAG-5	TNT/RDX/Al/wax (60/20/15/5)	1.65	7000	[28]
Torpex-4B	RDX/TNT/Al/Wax (40.5/37.5/18/4)	1.76	6700	[22]
–	RDX/Nitroguanidine/Al/Lecithin/Polywax 500 (22/45/16/0.2/17)	–	6900	[29]
–	HMX/EHA/Ozokerite/carnauba (83.0/2.5/3.63/10.87)	–	8150	[30]
–	RDX/Al/EHA/Ozokerite/carnauba (65.0/18.00.6/11.4)	–	7750	[30]
Pentastit	PETN/wax (93/7)	1.60	7720	[7]

Table 6 provides a summary of the most important wax additives used in explosives. Only for some compositions is it specified which modifier is used in which formulation (e.g. AFX-645). For the other modifying additives, only information was reached that it is used in explosive compositions. These compounds are usually present in the compositions in small amounts (less than 2%) and their role is usually to emulsify or stabilise the suspended solids during casting elaboration. On the physicochemical side of interactions at the microscopic level, modifiers can be classified as surfactants, film-forming additives and as emulsifiers. Only in the case of the composition labelled D2 in the literature was it possible to establish that it contains lecithin (emulsifier) and nitrocellulose (suspension stabiliser) in addition to wax. The lecithin nitrocellulose system is therefore relatively versatile as it shows compatibility with both carnauba wax (in mixture D2) and paraffin wax (in mixture D1). It can be assumed that the series of base waxes labelled D1 and D2 have a continuation but there is no literature information on this as yet.

Table 6. Emulsifiers, plasticisers [5]

Name	Composition, construction	Function
Aerosol TR70	Sodium bis-tridecyl sulfosuccinate	Emulsifier
Ganex WP-660	Polyvinylpyrrolidone	Film-forming additive
Ganex V-216	Vinylpyrrolidone-hexadecene copolymer	Emulsifier
Igepon T77	*N*-methyl oleoyl taurate	Emulsifier
Silwet L-7500	Copolymer of polyethylene oxide with polydimethylsiloxane	Surfactant
Pluronic	Family of non-ionic detergents. Copolymers of propylene glycol and polyethylene glycol.	Surfactant
Lecithin	Phosphatidylcholine	Emulsifier
D1 or PNL	Paraffin wax/NC/lecithin (84/14/2)	Base composition of waxes and desensitizing agents
D-2	Palm wax/NC/lecithin (84/14/2)	Base composition of waxes and desensitizing agents

4. Conclusions

Based on a review of the literature on waxes used in explosive compositions, the following conclusions can be drawn:

- Consumption of natural and synthetic waxes worldwide amounts to hundreds of thousands of tonnes per year. The use of waxes in explosive compositions represents a small fraction of total global consumption, but there is no indication that the use of natural waxes in explosive compositions will decrease dramatically in the next 10-20 years.
- Detailed data on the composition of waxes used in explosive compositions is much more difficult to access than information on the explosive used, its density, crystalline form, etc.
- The literature lists some 40 natural base and synthetic waxes used in explosive compositions. However, it can be assumed that 5-10 of these are realistically used. The most important of these are: palm wax, ceresin, Montana wax, Candelilla wax. Their use is due to their high availability, high physico-chemical durability and sufficiently high melting point.
- With the limit of energy storage in the structure of high-energy compounds being reached, progress is being made in modifying known explosive materials and compositions to, for example, reduce sensitivity to accidental initiation. On the basis of the results of the review performed, it can be concluded that there are currently no raw material alternatives for the use of waxes in explosive compositions.

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