United States Patent [19]

Slawinski

[11] **3,731,625**

[45] **May 8, 1973**

[54] PACKAGED EXPLOSIVE

[75] Inventor: **Frank E. Slawinski**, Tamaqua, Pa.

[73] Assignee: **ICI America Inc.**

[22] Filed: **May 14, 1971**

[21] Appl. No.: **143,328**

[52] **U.S. Cl.** ..... **102/24 R**

[51] **Int. Cl.** **F42b 3/00**

[58] **Field of Search** ..... 102/24 R

[56] **References Cited**

UNITED STATES PATENTS

3,049,079	8/1962	Eilo	102/24 R
3,342,132	9/1967	Partridge	102/24 R
3,472,166	10/1969	Dowling	102/24 R
3,504,628	4/1970	Pack et al.	102/24 R

FOREIGN PATENTS OR APPLICATIONS

1,186,331	4/1970	Great Britain	102/24 R

OTHER PUBLICATIONS

Materials Handbook, George S. Brady, Ninth Ed. 1963, McGraw-Hill TA403 B75 1963 C.2 page 709

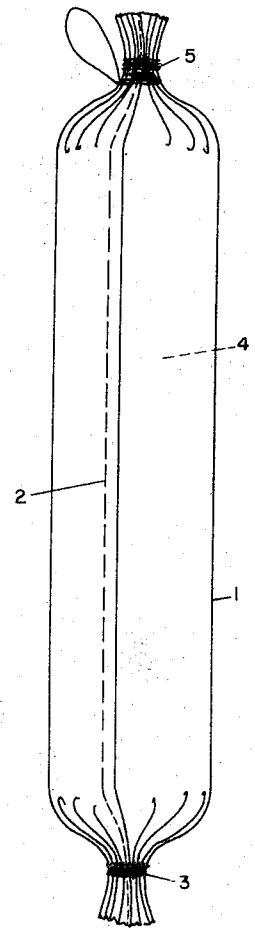
Primary Examiner—Verlin R. Pendegrass

Attorney—Kenneth E. Mulford and Roger R. Horton

[57] **ABSTRACT**

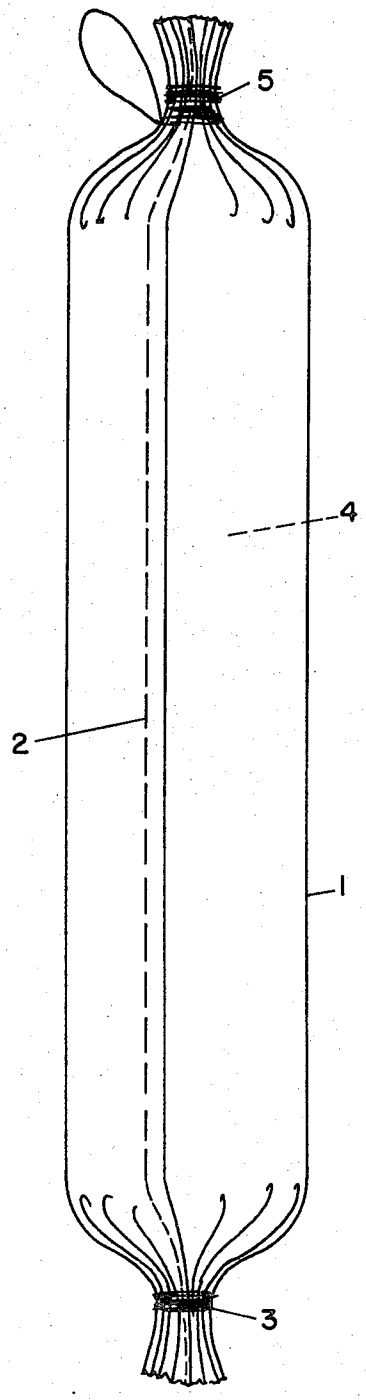
A skin-tight explosive not having an air space or sag, and a method of making it. An explosive containing a plasticizer-extractor is placed in a flexible polyvinyl chloride bag which has been plasticized with an extractable plasticizer. The air space or sagging bag which would normally form is eliminated due to the shrinkage of the bag.

15 Claims, 1 Drawing Figure



PATENTED MAY 8 1973

3,731,625



INVENTOR

Frank E. Slawinski

BY Richard D. Fuerle

ATTORNEY

PACKAGED EXPLOSIVE

Many explosives must be heated during their manufacture. They are usually immediately placed in a package and sealed. This procedure frequently causes the bag to wrinkle and sag or causes an air space to form at the top of the package due to contraction of the explosive as it cools. An air space or sag may also result due to the rearrangement of particles to mate better as they settle. This frequently happens when AN-FO (ammonium mitrate - fuel oil) is packaged, which is done at ambient temperatures. The air space or sag may also be caused by the coalescence of gases dissolved in the explosive or the absorption of gases into solid particles and this, too, may occur at ambient temperatures.

The presence of an air space or sag in the package is unattractive, which makes the product less salable, and an air space may prevent the propagation of the explosion from one container to the next when they are stacked in a borehole.

I have discovered a skin-tight explosive package and a method of making it. Due to an interaction between the container and the explosive, the container shrinks with the explosive forming a skin-tight package with no air space or sag. A flexible polyvinyl chloride (PVC) film is plasticized with an extractable plasticizer and formed into a bag. An explosive which contains a plasticizer-extractor; preferably a solvent for the plasticizer such as most oils, is placed in the bag and the bag is sealed. Gradually, the bag shrinks as the plasticizer in the bag is allowed to be extracted into the plasticizer-extractor in the explosive which may migrate through the plastic to form a light film on the bag.

In addition to the elimination of the air space and sag, the packaged explosive of this invention has superior elasticity, toughness, and memory which enable it to be dropped into boreholes containing water without rupturing. The shrinkage of the polyvinyl chloride bag also puts pressure on the explosive which may cause the particles in an explosive such as AN-FO to rearrange themselves to give the explosive a higher density. This may be desirable as it will enable the explosive to sink better in a water-filled borehole.

The accompanying drawing is a side view of a certain presently preferred embodiment of this invention.

In the drawing, a sheet of flexible polyvinyl chloride which has been plasticized with an extractable plasticizer is formed into a tube **1** by making a side lap seal **2**. One end of the tube is tied with a cord **3** to form a bag and the bag is filled with an explosive **4** containing a plasticizer-extractor. The other end of the bag is then sealed by tying it with a second cord **5** to form the packaged explosive.

While the packaged explosive of FIG. **1** is preferred because of its strength, low cost, and ease of manufacture, other types of bags may also be used. Examples include blow-molded shells, seamless tubing, vacuum-drawn containers, and spiral-wound shells. The bag preferably is cylindrical and has a diameter of about 1 to 12 inches and a length of about 6 to 45 inches.

Although the polyvinyl chloride may be of any flexible thickness, a thickness of at least about 4 mils and up to about 50 mils is generally suitable. Preferably, for the best explosive packages, the thickness should be between about 6 and about 20 mils.

The polyvinyl chloride bag is plasticized with a sufficient amount of an extractable plasticizer to (1) obtain the desired degree of shrinkage when the plasticizer is in part extracted and (2) leave enough plasticizer unextracted to keep the bag flexible. I have found that the amount of plasticizer in the polyvinyl chloride should be about 20 to about 60 percent (all percentages herein are by weight) of the polyvinyl chloride to obtain the best results.

The plasticizer must be extractable. Examples of plasticizers which are extractable in mineral oil and most other oils and are therefore preferred include dioctyl phthalate, diisooctyl phthalate, diisodecyl phthalate, trichloroethyl phosphate, trioctyl phosphate, tri-2-ethylhexyl phosphate, octyl-diphenyl phosphate, decyl-diphenyl phosphate, cresyldiphenyl phosphate, tricresyl phosphate, dioctyl adipate, polyethylene glycol di-2-ethyl-hexoate, and mixtures thereof. Certain alkyl aryl phosphates may also be used. Table 1 gives the percent that various plasticizers were extracted from a film after the film was soaked in S.A.E. 20 oil for 10 days at 23°C.

TABLE 1

Plasticizer	% Extracted
Dioctyl phthalate	17.3
Tri-2-ethylhexyl phosphate ($[C_4H_9CH(C_2H_5CH_2O]_3P=O$) sold under the trademark "Flexol TOF" by Carbide and Carbon Chemicals Co.	29.1
Octyl-diphenyl phosphate sold under the trademark "Santicizer 141" by Monsanto Chemical Co.	14.1
Tricresyl phosphate	6.3
Dioctyl adipate	20.6
Polyethylene glycol di-2-ethyl-hexoate ($C_7H_{15}COOCH_2(CH_2OCH_2)_3CH_2OCOC_7H_{15}$) sold under the trademark "Flexol 4GO" by Carbide and Carbon Chemicals Co.	25.2
A high-boiling liquid, sp. gr. 0.9564, boiling point 255°C. (5 mm. Hg), flash point 420°F., practically insoluble in water, sold under the trademark "Flexol 8N8" by Carbide and Carbon Chemicals Co.	12.8

The above table was in part obtained from "The Stabilization of Polyvinyl Chloride" by Chevassus Broutilles, page 263.

Table 2 gives the percent extractability in mineral oil of various phthalate plasticizers. The plasticizer concentrations are at 50 parts per hundred of resin.

TABLE 2

Phthalate	% Extractable
Dioctyl	1.0
Diisooctyl	1.3
Diisodecyl	2.4
Various linear phthalates made from Conoco, Ethyl, and Monsanto alcohols	3.4 to 5.1

The above table was obtained from the November, 1970 issue of "Modern Plastics," page 78.

Table 3 gives the percent extraction of various plasticizers in kerosene. A 40 mil PVC film was used with a plasticizer concentration of 67 p.h.r. (parts per hundred of resin).

TABLE 3

Plasticizer	% Extraction
Dioctyl phthalate	34
Trichlorethyl phosphate	6.7
Trioctyl phosphate	74
Octyl-diphenyl phosphate[1]	7.3
Decyl-diphenyl phosphate[2]	6.7
Cresyl-diphenyl phosphate	2.1
Tricresyl phosphate	1.3

1. Sold by Monsanto Chemical Co. under the trademark "Santicizer 141."
2. Sold by Monsanto Chemical Co. under the trademark "Santicizer 148."

The above table was obtained from the Jan. 29, 1971 issue of "Chemscope," page 18. The differences in extractability of dioctyl phthalate between Tables 1, 2, and 3 may be due to experimental differences such as the amount of plasticizer originally in the film.

At least about 0.1 percent of the plasticizer should be extracted to obtain a noticeable amount of shrinkage. Preferably, about 3 percent to about 40 percent of the plasticizer is extracted to obtain a significant amount of shrinkage without leaving the polyvinyl chloride bag inflexible and brittle.

Table 4 gives the percent contraction of 7" MD (machine-direction) by 5" CD (cross-direction) sheets of PVC film after 1 week and 1 month of immersion in various solvents, primarily oils. "KDA–2076" is a product designation of Union Carbide for a 12 mil PVC film plasticized with 33.5 percent dioctyl phthalate and having a density of 1.225 gms./cc. "KDA–2109" is a Union Carbide product designation for a 20 mil PVC film having a density of 1.215 gms./cc. plasticized with 33.8 percent "Flexol 10—10" (a Carbide and Carbon Chemicals Co. trademark for diisodecyl phthalate).

TABLE 4

Solvent	"KDA–2076" 1 Week MD	"KDA–2076" 1 Week CD	"KDA–2076" 1 Month MD	"KDA–2076" 1 Month CD	"KDA–2109" 1 Week MD	"KDA–2109" 1 Week CD	"KDA–2109" 1 Month MD	"KDA–2109" 1 Month CD
Alcaid Oil[1]	1.3%	1.2%	2.7%	2.6%	0.9%	.2%	1.3%	1.8%
Atreol 34[2]	2.3	2.6	3.6	3.8	1.9	1.8	2.3	2.6
Klearol[3]	2.3	2.6	4.0	4.4	1.3	2.6	2.3	3.2
Castor Oil	2.3	2.6	3.6	3.8	1.9	2.6	3.6	3.8
Cod Liver Oil	1.9	3.8	2.7	5.6	3.6	4.4	5.4	5.0
Corn Oil	4.4	3.8	5.4	5.0	3.6	3.8	5.4	6.2
Corvus[4]	1.3	1.2	2.3	2.6	0.9	0.6	2.3	2.6
Compression Oil	1.9	1.8	3.1	3.2	1.9	1.8	2.7	3.2
DFO No. 2	3.6	3.8	5.4	5.6	2.7	3.8	4.4	5.0
Ebony B[5]	0.0	0.6	0.4	1.2	0.4	0.6	0.4	0.6
Gasoline	9.0	8.8	9.0	8.8	8.0	9.4	9.0	10.0
Glycerine	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0
Glycol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kerosene	4.4	5.0	6.3	7.6	5.4	5.6	7.1	7.6
Linseed Oil	3.6	3.8	5.4	6.2	3.6	5.0	4.4	5.6
Mineral Spirits	6.3	6.2	8.0	8.8	6.3	6.8	7.1	7.6
Motor Oil No. 10	0.9	1.2	1.9	2.6	0.9	1.2	2.7	2.6
Motor Oil 10–30	1.9	1.22.7		2.6	1.3	1.8	1.9	2.6
Nitromethane	9.0	7.6	10.1	6.2	7.8	5.0	7.1	5.0
NG (PGD — 90% glycol — 10% (glycerine)	6.7	6.9	10.0	10.9	7.0	50	8.8	9.3
Olive Oil	2.7	3.2	4.4	5.0	2.7	3.8	4.0	5.0
Paraffin Oil	1.3	1.8	3.1	3.8	1.3	1.8	1.8	2.6
Peanut Oil	3.1	3.2	4.4	5.0	3.1	4.4	4.4	5.0
Rustoleum Thinner[6]	6.3	6.2	7.1	7.6	5.4	7.6	7.1	7.6
Rabtex[7]	0.4	0.6	1.9	1.2	0.0	0.6	0.8	0.6
Safflower Oil	3.6	3.8	5.4	5.0	2.7	3.8	4.4	5.6
Soybean Oil	3.1	3.2	4.4	5.0	2.7	3.8	4.4	5.6
Actinol[8]	3.6	4.4	4.4	5.0	4.0	3.8	4.4	5.0
Turpentine	5.4	6.2	6.3	6.8	5.4	6.2	7.1	7.6

1. Texaco, Inc., trademark for lubricating oil.
2. Atlantic Richfield Co. trademark for mineral oil.
3. Witco Chemical Co. trademark for mineral oil.
4. Texaco, Inc., trademark for lubricating oil.
5. Atlantic Richfield Co. trademark for lubricating oil
6. Rustoleum Corp. trademark for fish oil.
7. Texaco, Inc., trademark for lubricating oil.
8. Arizona Chemical Co. trademark for a fatty acid fraction of tall oil.

Fuel oil, mineral oil, lubricating oil, kerosene, nitroalkanes from C_1 to C_3, and nitroglycerins are preferred as they are the most useful in formulating explosives.

Table 5 shows the percent contraction of 5" CD by 7" MD sheets of PVC film immersed for various periods of time at 70°F. and 90°F. in a mineral oil sold under the trademark "Atreol 34" by the Atlantic Richfield Co. "KDA–2030" is Union Carbide's product designation for 8 mil PVC plasticized with 33.7 percent dioctyl phthalate and having a density of 1.237 gms./cc. "KDA–2078" is Union Carbide's product designated for 12 mil PVC plasticized with 30 percent dioctyl phthalate and having a density of 1.251 gms./cc. "Toywrap" is Transilwrap Co.'s product designation for 2-mil plasticized PVC.

TABLE

Film	1 Day 70°F	1 Day 94°F	3 Days 70°F	3 Days 94°F	1 Week 70°F	1 Week 94°F	1 Month 70°F	1 Month 94°F
KDA–2076 MD	1.4%	1.7%	1.7%	3.6%	3.6%	3.6%	4.4%	5.3%
CD	2.0%	2.0%	1.2%	2.4%	2.4%	2.4%	5.0%	6.2%
KDA–2030 MD	1.4%	1.7%	1.7%	2.7%	1.7%	3.6%	3.6%	4.4%
CD	2.0%	2.0%	2.4%	2.4%	2.4%	4.0%	5.0%	6.2%
KDA–2078 MD	1.4%	1.7%	.86%	1.7%	1.7%	1.7%	2.7%	3.6%
CD	2.0%	2.0%	1.2%	2.4%	1.2%	2.4%	2.4%	2.4%
Toywrap MD	3.6%	2.9%	3.6%	3.6%	4.4%	3.6%	5.3%	4.4%
CD	1.2%	2.0%	1.2%	2.5%	1.2%	2.4%	2.4%	3.8%

Table 6 shows the percent contraction of 5" by 7" sheets of PVC film after immersion at 70°F. and 104°F. for various periods in "Atreol 34" mineral oil. "Regalite" is the product designation of Tenneco Chemical Co. for a plasticized PVC about 10 mils thick.

TABLE 6

PVC	Direction	1 day, percent 70° F.	1 day, percent 104° F.	2 days, percent 70° F.	2 days, percent 104° F.	1 week, percent 70° F.	1 week, percent 104° F.	2 weeks, percent 70° F.	2 weeks, percent 104° F.	1 month, percent 70° F.	1 month, percent 104° F.
Regalite	MD	0	2.86	0	2.86	0	4.43	0.86	5.29	1.86	6.29
	CD	1.2	1.2	1.2	2.0	1.2	2.6	1.2	4.0	2.6	5.0
KDA 2076	MD	0.86	2.86	0.86	2.86	1.4	5.29	2.86	7.1	3.6	8.0
	CD	1.2	1.2	1.2	2.6	2.0	5.0	2.6	6.2	4.0	7.4
KDA 2030	MD	0	1.9	0	1.9	1.4	3.6	1.9	5.3	1.9	6.3
	CD	1.2	1.2	1.2	1.2	1.2	4.0	2.6	5.0	4.0	6.2

Virtually any explosive containing about 0.1 to about 80 percent extractor for the plasticizer may be used in this invention. Preferably the explosive should contain about 1 percent to about 10 percent plasticizer-extractor in order to extract the plasticizer in amounts previously described. Dynamite, AN-FO, slurries, and water-in-oil emulsions are four common, suitable explosives which may contain a plasticizer-extractor, usually an oil. Of the four, water-in-oil emulsions are preferred because they exhibit the greatest amount of noticeable product shrinkage and they cause the greatest amount of bag expansion in the polyolefin and copolymer bags commonly used.

A dynamite composition may comprise, for example, 1 pbw (part by weight) inorganic oxidizer salt, about 0.3 to 8 pbw nitroglycerin, nitroglycol, or mixtures thereof, and up to about 0.6 pbw gelatinizing agent such as nitrocotton. Various fuels may also be included.

AN-FO compositions contain ammonium nitrate prills and liquid hydrocarbon fuel, for example, about 78 to 97 percent ammonium nitrate and about 2 to 12 percent liquid hydrocarbon fuel, such as fuel oil which is inexpensive. The compositions may also contain surfactants, metals, additional fuels, sensitizers, and other substances.

An oil-containing slurry explosive may comprise, for example, about 10 to about 70 percent inorganic oxidizer salt, about 10 to about 30 percent water, about 1 to 30 percent oil, and sufficient oil thickener to keep the oil from separating. Other fuels, metals, sensitizers, etc., may also be used.

A water-in-oil emulsion explosive may comprise, for example, about 1 to about 10 percent carbonaceous fuel (e.g., an oil), about 55 to about 87 percent oxidizer, about 0.1 to about 15 percent sensitizer, about 10 to about 25 percent water, about 1/2 to about 2 percent emulsifier, and sufficient gas to give the explosive a density of about 0.9 to about 1.40 gms./cc. (See Bluhm U. S. Pat. No. 3,447,978).

Table 7 shows the shrinkage and effectiveness of AN-FO explosives in PVC bags after various intervals. The PVC bag used was a side lap sealed bag as shown in the accompanying drawing made from "KDA–2076" PVC. Product A is 90 percent whole and ground AN prills, 4 percent No. 2 diesel fuel oil, and 6% al. granules. Product B is 94.25 percent whole Al ground AN prills and 5.75 percent No. 2 diesel fuel oil. The samples were shot with 4" high-velocity gelatin in 5" × 12" cartridges.

TABLE 7

Time	Product A Fresh	Product A 1 week	Product A 1 month	Product A 6 months	Product B Fresh	Product B 1 week	Product B 1 month	Product B 6 months
Diameter of cartridge (inches):								
Top:								
1	4 59/64	4 53/64	----	4 53/64	4 49/64	4 53/64	----	----
2	4 53/64	4 59/64	----	----	5	4 55/64	----	4 59/64
Bottom:								
1	4 59/64	4 59/64	----	4 48/64	4 58/64	4 55/64	----	----
2	5	4 62/64	----	----	5 3/64	4 62/64	----	4 49/64
Length of cartridge (inches):								
1	34	34 1/4	----	33 1/4	34 3/4	----	----	----
2	35	34 1/2	----	----	35	35	----	33 3/4
Density (gms./cc.):								
1	1.146	1.184	1.180	1.207	1.167	1.210	----	----
2	1.180	1.177	1.206	----	1.159	1.154	1.147	1.164
Velocity (f.p.s.) distance from power primer:								
1"–7"				10,870				10,870
5"–11"				9,800				10,200

The above table shows that the cartridge not only shrank but also increased in density.

Table 8 gives the density and velocity when shot of various samples of two water-in-oil emulsion explosives prepared according to Bluhm U.S. Pat. No. 3,447,978 after various periods of storage at 90°F. and ambient temperatures. All samples had a density of 1.15 gms./cc. when prepared. Emulsion A contained 2.5 percent mineral oil. Emulsion B contained 0.5 percent mineral oil. The samples were shot with 3" high-velocity gelatin primer in 3" × 15" cartridges of "K-DA–2076" PVC.

TABLE 8

Age of Sample		Emulsion A Ambient	Emulsion A 90°F.	Emulsion B Ambient	Emulsion B 90°F.
1 Week	Velocity (fps)	18520	19050	16670	17090
	Density (gms./cc.)	1.203	1.203	1.207	1.203
3 Months	Velocity (fps)	18520	18520	16025	14425
	Density (gms./cc.)	1.223	1.197	1.260	1.267
5 Months	Velocity (fps)	18820	18520	16305	10560
	Density (gms./cc.)	1.213	1.217	1.220	1.270
6 Months	Velocity (fps)	19050	19230	14960	failed
	Density (gms./cc.)	1.210	1.210	1.257	1.287

The above table shows the increase in density of each sample from its original 1.15 gms./cc.

What is claimed is:

1. A skin-tight packaged explosive composition free of air spaces and sags contained in a sealed, flexible, plasticized polyvinyl chloride film container, said container characterized in that a portion of the plasticizer in said polyvinyl chloride film container is extracted by said explosive composition, said explosive composition characterized in that it contains an extractor for said plasticizer in contact with said container.

2. A packaged explosive according to claim 1 wherein said plasticizer is selected from the group consisting of dioctyl phthalate, diisooctyl phthalate, diisodecyl phthalate, trichloroethyl phosphate, trioctyl phosphate, tri-2-ethylhexyl phosphate, octyl-diphenyl phosphate, decyl-diphenyl phosphate, cresyl-diphenyl phosphate, tricresyl phosphate, dioctyl adipate, polyethylene glycol di-2-ethyl-hexoate, and mixtures thereof.

3. A packaged explosive composition according to claim 1 wherein said explosive is a dynamite.

4. A packaged explosive composition according to claim 1 wherein said explosive composition is AN-FO.

5. A packaged explosive composition according to claim 1 wherein said explosive composition is a slurry.

6. A packaged explosive composition according to claim 1 wherein said explosive composition is a water-in-oil emulsion.

7. A packaged explosive composition according to claim 1 wherein said polyvinyl chloride film contains about 20 to about 60 percent plasticizer.

8. A packaged explosive composition according to claim 1 wherein said container is a lap side sealed bag.

9. A packaged explosive composition according to claim 1 wherein said extractor is a solvent for said plasticizer.

10. A packaged explosive composition according to claim 9 wherein said extractor is an oil.

11. A packaged explosive composition according to claim 9 wherein said solvent is selected from the group consisting of fuel oil, mineral oil, lubricating oil, kerosene, nitroalkanes from C_1 to C_3, and nitroglycerine.

12. A packaged explosive composition according to claim 1 wherein said polyvinyl chloride film is at least 4 mils and less than 50 mils thick.

13. A packaged explosive composition according to claim 11 wherein said polyvinyl chloride film is about 6 to about 20 mils thick.

14. A packaged explosive composition according to claim 1 wherein said explosive composition contains about 0.1 to about 80 percent extractor.

15. A packaged explosive composition according to claim 14 wherein said explosive composition contains about 1 to about 10 percent extractor.

* * * * *