

Study on the Types of Propellants and Stabilizers Used in Shotgun Cartridges from Various Brands

Noor Khairatul Azni Mat^a, Abd Aziz Ishak^a, Pua Hiang^a

^a Forensic Science Programme, Faculty of Health Sciences, Universiti Kebangsaan Malaysia, Kuala Lumpur, Malaysia.

ABSTRACT: Cases involving shotgun occur frequently in Malaysia. Propellants are always found at the crime scenes. This research is conducted to classify the propellants based on their physical properties, types of propellant either nitrocellulose (NC) or nitroglycerine (NG) and types of stabilizer used according to their brands and shot sizes. Brands of manufacturer that are used in this research are SME with shot size 6, Winchester with shotsize 6, 7 ½ and 8, Fiocchi with shot size 7 and Remington with shot size 6. A stereo microscope is used to observe physical properties such as size and shape of the propellant. Colour of the propellant was compared against Munsell System Colour Chart. To determine the type of propellant, either nitrocellulose or nitroglycerine, TLC method is used, solvents that are used in this method are toluene and ethyl acetate with the ratio 9:1. These solvents act as a mobile phase. Modified reagent Griess is also used to stain the NC or NG with orange spot. It was found that propellant from SME and Fiocchi is SB propellant while Winchester and Remington is DB propellant. To determine the types of stabilizers, UPLC is used. Acetonitrile and pure water were used in a 6:4 ratio. DPA has a retention time around 3.817 minutes while EC around 4.786 minutes. It was found that all samples have DPA stabilizers while only Remington and SME 6 have EC stabilizers. Thus, stabilizers of the propellant cannot be discriminated. Based on the results of physical properties, it was found that the propellants can be discriminated as there was significant difference between the brands.

Keywords : propellant; double base; single base; diphenylamine; ethyl centralite; Thin Layer Chromatography (TLC); Ultra Performance Liquid Chromatography (UPLC).

Introduction

Firearms are tools that use explosive ammunition and can explode. Examples of firearms are rifles, revolvers, machine gun, submachine gun, shotgun, pistol and etc. The owner and the user of the firearms must apply for a valid license as provided under Firearms Act 1960 [1]. When a shot is released, there must be a sign left at the crime scene. The sign can be a unique characteristic or can be called as 'fingerprints' which can be used to identify the firearms used. In contrast, shotgun does not have this unique feature because shotgun has a smooth barrel [2]. Thus the study of the morphology, composition and physical properties of propellant, study of different types of stabilizers, ward and diameter and weight of the pellet should be conducted.

Different manufacturer will produce different brands and different types of stabilizer. Propellants can be classified according to their physical properties, shapes, sizes, colours, and modification made on their surface [3]. This

study involved four different brands which are SME, Winchester, Fiocchi and Remington. Shotgun cartridges were obtained from the market around Kuala Lumpur and Selangor with the permission from Royal Malaysian Police. Samples obtained have shot sizes of 6, 7, 7½ and 8.

The basic components of a cartridge are a ward, propellants, bullet, cartridge case, primer and shotsize. Depending on the propellant, whether chemical or mixture of chemicals which when ignited will produce large quantities of gas. This gas when confined in the barrel and are behind bullet, then it will be as a driver to drive the bullet out of the muzzle.

Propellant can be categorised into single base and double base. Single base containing nitrocellulose (NC) as the main explosive material and the double base contains both the NC and nitroglycerine (NG) [4]. NG is a nitrate ester and has been extensively used in the manufacturing of explosives and solid type

propellant. The aim of use of this stabilizer is to increase the power of ballistic, hydrophobic tendency, energy and soften the propellant. However, the NG also use as a main component of smokeless of gunpowder. Usually NC widely used in the manufacture of varnish, celluloids pharmaceutical and industrial films [5].

Stabilizer is an additive in the propellants acting as a primary material that remove decomposition products of NC and NG. Examples of stabilizers that are used in manufacturing ammunitions are ethyl centralite and methyl centralite [6,7]. If the product of decomposition is not removed, it will act as a catalyst and cause further decomposition where it will reduce the lifespan of an ammunition and self ignition can occur from increasing degradation product of catalytic effect automatically [8].

EC will remove oxide from degradation products by acting as a weak base and reacts with decomposition to form the nitro and nitro derivative. Diphenylamine (DPA) is another example of stabilizers that are commonly found in single base propellants. Concentration that is commonly used is only 1% and both are often easily found in ammunition [6,9].

This study compares the stabilizers and the physical properties of propellants used in shotgun cartridges with shot sizes 6, 7, 7½ and 8 which are derived from the four different manufacturers.

Materials and Method

Sample preparation

Propellants from four different manufacturers with their shot sizes 6, 7, 7½ and 8 were used. All samples were obtained from Royal Malaysian Police (RMP) Forensic Laboratory. Propellant was removed under the supervision of police and stored in plastic containers and labeled. Each brand of manufacturer for one type of shot size was sampled seven times from seven different cartridges. Propellant samples from different cartridges were stored in different plastic containers, labeled as 1, 2, 3, 4, 5, 6, and 7, respectively.

Sampling

Physical properties of propellants such as colour, shape, and size, propellant was observed under a stereo microscope. Pictures were taken using a stereo microscope camera for further observation. Colour of the propellant was compared with the Munsell Color System. Thin Layer Chromatography (TLC) was used to study the type of propellant. This method was used to test the presence of NC or NG in propellants.

Propellant sample was taken and placed in a beaker. Then 5 drops of acetone was added to dissolve the propellant. Sample solution placed at the middle line on aluminum sheets using a capillary tube and soak in a solution containing a mixture of toluene and acetic acid with ratio is 9:1. Aluminum sheet was left for an hour and when removed, the furthest distance the solvent moves were marked. TLC sheets were dried and sprayed with sodium hydroxide and heated on a hotplate (100 °C) for 10 minutes. After that, the TLC sheets were sprayed with *Griess* reagent. Each measurement was recorded.

Propellant samples were prepared from three cartridges that come from different manufacturers but same shot size. Each cartridge was prepared three times. The sample was weighed for about 0.05 g and dissolved in acetonitrile and pure water with a ratio of 6:4. Once the sample was dissolved, they were further diluted in 10 mL volumetric flask and subsequently injected at 2 mL into each glass vial using a syringe connected to a 0.2 µm membrane filter. Glass vials were placed in UPLC instrument for sample injection preparation. 5 µL of the overall total of 2 mL sample was injected into the UPLC sample inlet. Standards of diphenylamine and ethyl centralite also appeared in the peak but were excluded in further analysis process [10].

Results and Discussion

The results of the physical properties of propellants such as colour and shape were shown in Table 1 while the results of size of propellant as shown in Table 2.

Table 1: Colour and shape of the propellants

Manufacturers	Shot sizes	Colour	Shape
Winchester	6	<i>Greenish Gray</i> (5 GY 6/1)	A mixture of an irregular flakes, flat and balls (minor)
	7 ½	<i>Greenish Gray</i> (5 GY 6/1)	A mixture of an irregular flakes, flat and balls (minor)
	8	<i>Greenish Gray</i> (5 GY 6/1)	A mixture of an irregular flakes, flat and balls (minor)
SME	6	<i>Dusky yellow green</i> (5 GY 5/2)	Rounded and distorted
	7 ½	<i>Grayish Green</i> (5 G 5/2)	Rounded and distorted
	8	<i>Moderate yellowish green</i> (10 GY 6/4)	Rounded and distorted
Fiocchi	7	<i>Dark Yellowish Green</i> (10 GY 4/4)	Irregular rectangle, flat
Remington	6	<i>Olive Black</i> (5 Y 2/1)	Irregular rounded flakes

Table 2: Size of propellants

Manufacturers	Shot sizes	Cartridges	Minimum (mm)	Maximum (mm)
SME	6	a	7.065	7.246
		b	6.899	8.319
		c	6.804	6.878
		d	6.908	7.230
		e	7.202	7.241
		f	6.738	7.053
		g	6.863	7.091
		Mean	6.916	7.294
		S.deviation	0.159	0.471
SME	7 ½	a	5.362	6.161
		b	5.446	5.977
		c	5.703	6.408
		d	5.253	6.030
		e	5.762	5.778
		f	5.267	5.341
		g	5.541	5.965
		Mean	5.476	5.951
		S.deviation	0.683	0.332
SME	8	a	6.901	7.501
		b	6.649	7.395
		c	7.582	7.654
		d	6.738	7.996
		e	7.427	7.818
		f	7.044	7.669
		g	7.045	8.042
		Mean	7.055	7.725
		S.deviation	0.343	0.240
Winchester	6	a	0.823	1.388
		b	0.714	2.713
		c	2.881	7.950
		d	2.514	5.270
		e	2.961	4.973
		f	2.730	5.311
		g	3.024	4.376
		Mean	2.235	4.569
		S.deviation	1.016	3.748
Winchester	7 ½	a	1.989	8.946
		b	2.303	5.582
		c	2.592	5.432
		d	3.099	5.359
		e	2.907	5.674
		f	2.698	6.970
		g	2.171	5.050
		Mean	2.537	6.145
		S.deviation	0.402	1.378
Winchester	8	a	2.945	5.924
		b	3.360	5.487
		c	2.440	5.695
		d	2.939	6.061
		e	1.807	4.248
		f	2.160	6.032
		g	2.377	5.310
		Mean	2.575	5.537
		S.deviation	0.533	0.634

Table 2 (cont.)

Manufacturers	Shot sizes	Cartridges	Minimum (mm)	Maximum (mm)
Fiocchi	7	a	4.806	4.283
		b	4.809	4.872
		c	5.979	6.013
		d	4.910	5.699
		e	5.726	6.034
		f	5.764	6.188
		g	5.897	6.171
		Mean	5.413	5.609
		S.deviation	0.543	0.742
Remington	6	a	5.437	5.641
		b	5.530	5.598
		c	5.157	5.162
		d	5.362	5.755
		e	5.655	5.754
		f	5.430	5.479
		g	5.216	5.414
		Mean	5.398	5.543
		S.deviation	0.172	0.211

Propellant usually has a range of colors from black to gray. This is because the propellant has composite and composite material modified that contribute to variations in color and appearance. The material used in the manufacturing of propellant powders such as aluminum and other metals give a dark gray to black colour. However, other additives can also provide the range of variations in color from red to green to black [11].

In the manufacturing of solid propellant, the rate of combustion is perpendicular to the surface area at all times. The time taken by the propellant to burn a compact mass will be longer when compared with propellants that have cylinder elongated holes like a tube. Hence, burning propellant fully depend on their shape [12].

Table 3 shows the results of TLC. Note that SME and Fiocchi brands are single base while Winchester and Remington are double base.

Table 3: Area under the graph for DPA stabilizer

Manufacturer	Shot sizes	Mean	Concentration (mg/mL)
SME	6	3244632	0.042
SME	7½	3006525	0.039
SME	8	2172543	0.027
Winchester	6	3242799	0.043
Winchester	7½	2602638	0.034
Winchester	8	2637810	0.035
Fiocchi	7	3490817	0.044
Remington	6	282261	0.010

To observe chemical reactions of nitrate esters found in the NC and NG, the chemical reaction used a modified *Griess* reagent with a mixture of α -naftol 0.5 g in 165 mL 30% acetic acid and 1.0g sulfanilic acid in 100ml of 30% acetic acid. This result shows the presence of the orange spot. The theory using a visualization method of Griess reagent is nitro group in explosives material will be hydrolyzed to nitrite ions when subjected to the base of 1M solution of sodium hydroxide and heated to 100 °C. Next, when the reagent is sprayed on TLC aluminum sheets at this stage nitro amine and nitrate esters will react and orange color is formed. This is because sulfanilic acid found in the *Griess* reagent reacts with nitrite ion and form a diazonium salt. Next, diazonium salt formed will react

with azo agent in α -naftol and gives orange color [13].

This separation is dependent on relatively tendency of the stationary phase by the mobile phase. Solutes with high retain will remain in its original position and the solutes with low retain move up through the mobile phase on the same sheet. Therefore the observed points of orange color is nitrate esters, NG. While giving the Rf value 0.00 is considered as NC [14].

Propellant from manufacturer of SME, Winchester, Fiocchi and Remington has a DPA stabilizer, Table 3. Only propellant from SME 6 and Remington 6 shows the presence of EC, Table 4.

Table 4: Area under the graph for EC stabilizer

Manufacturer	Shot sizes	Mean	Concentration (mg/mL)
SME	6	1748593	0.04
Remington	6	516180	0.015

The use of stabilizers such as DPA is available in various conditions in which the sample is to characterize propellant powder which not only depends on the brand but also the way of the storage and thermal history by the manufacturer [15]. This is consistent and supported by Zayed *et al.* [16] which states that these stabilizers help in propellant chemically. Stabilizer does not stop the degradation but to prevent the catalytic reaction by removing the result of degradation products such as NO, NO₂, HNO₂ and HNO₃.

For quantitative calculations, the area under the graph was calculated using UPLC instrument. It was found that the area under the graph of DPA was higher than EC, Table 4, indicating that the stabilizers were used in high quantities in the manufacturing of propellants to help extend the life span of a shotgun cartridge.

Conclusion

Colour of propellant showed differences for different brands. Internal comparison between the same brands showed that propellant could not be discriminated. Further comparison of the shape of the propellants could be used. This research shows the physical properties of the propellant could discriminate SME brands, Winchester, Fiocchi and Remington. SME and Fiocchi were single base while Winchester and Remington were double base propellant. Qualitative comparisons could not discriminate propellant of SME brand, Winchester, Fiocchi and Remington. However, a quantitative comparison can differentiate propellants which originated from the SME, Winchester, Fiocchi and Remington regarding to the area under the peak.

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Additional information and reprint request:

Pua Hiang

Email: hpuu@ymail.com

Forensic Science Programme

Faculty of Health Sciences

Universiti Kebangsaan Malaysia

Kuala Lumpur, Malaysia

Tel: 016-2879081