

Molotov cocktail protection – protective clothing material for emergency forces

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ABSTRACT

In order to better protect emergency personnel, a suitable material was sought that would meet various requirements. To achieve this, a project was carried out by the Saxon Textile Research Institute e. V. (STFI), Germany and the Institut für Textiltechnik (ITA) of RWTH Aachen University, Germany, called “Molotov cocktail protection – protective clothing material for emergency forces”. First, suitable fiber mixtures were selected and then tested for a high accuracy of fit. Afterwards, specially designed fabrics were developed and produced to realize a smooth surface. In addition, a coating for high hydrophobia was established. To examine these newly developed fabrics, a test procedure was developed and modified. Results show correlations between fiber selection as well as yarn and fabric construction with the resulting fabric properties. Findings can be given in the form of technological and product-related recommendations.

Keywords

police forces,
Molotov cocktail,
heat shrinkage,
wearing comfort,
blended yarns,
reinforcing fabrics

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1 Introduction

In recent years, the population’s propensity to violence has grown enormously, with police and fire brigade forces being increasingly affected. The attacks are mostly carried out by political extremists, who increasingly use Molotov cocktails. A Molotov cocktail is a bomb made of oil and petrol as well as some high viscose and sticky additives (e.g. coffee grounds) that causes flames to form and heat to develop at between 800 °C and 2000 °C. Thus, the temperature is high for a short period of time. This means that for a short time the temperature is higher than the heat load of firefighters during a fire operation [1-3].

During a street protest in May 2020, a group of police officers were attacked with a Molotov cocktail [4]. Also in May and the following month, several attacks took place on German police headquarters [5,6].

Irish police officers were also attacked with incendiary bottles during a bomb raid [7]. These are just a few examples of Molotov cocktail attacks in the last year. Despite the high incidence and potential danger, these attacks have not yet been specified separately, but are only recorded as throwing attacks [8].

In Fig. 1, the long-term development of cases and victims of German police officers is shown. The registered cases of violent offences are compared to the reported injuries of the police officers. On the y-axis, the number of incidents is plotted against the years on the x-axis. In 2020, there were 38,960 cases of violent offences – compared to the average of the last eight years (35,120 cases), this represents an increase of 9.10 %. In the 38,960 reported acts of violence, 84,831 police officers were injured. The number of reported injuries also increased by 19.10 % compared to the average of the last nine years (68,626 cases). The increase since 2012 in the number of violent offences against police officers is + 20.4%, while the number of police officers recorded as victims is even significantly higher at + 42.0% [9].

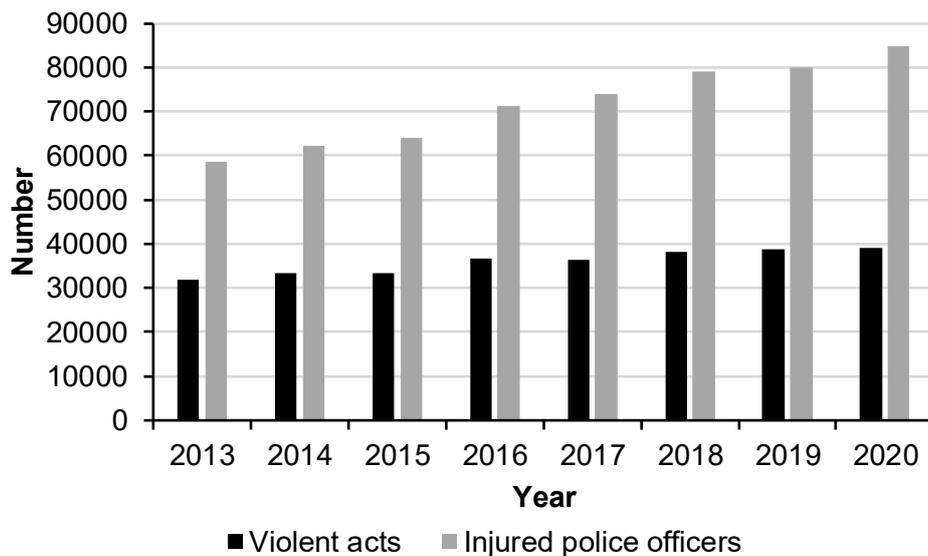


Fig. 1 Development of violent attacks on German police officers [9].

An overview of the types of attacks and the resulting injuries cannot be obtained from the statistics of the Federal Criminal Police Office (German: Bundeskriminalamt – BKA), Germany. There are also statistics by State Criminal Police Office (German: Landeskriminalamt – LKA) and Federal Ministry of the Interior and Community, Germany. However, they collect separate statistics, so that the number of violent attacks caused by incendiary devices can hardly be recorded. Some statistics are listed below:

- In the BKA study “Politically motivated confrontational violence – confrontations between left- and right-wing oriented actors in the years 2011-2012”, a total of 4,649 confrontational offences recorded by the police were evaluated. In 86 of 2,159 cases (4%), incendiary/explosive weapons were used as the means of committing the crime [10].
- According to the NRW study on “Violence against Police Officers”, 12,862 police officers experienced attacks against them by throwing pyrotechnics or similar in 2011. Even if the percentage of these acts is assessed as rather rare, such acts are assessed as considerably stressful [11].
- The LKA Saxony regularly evaluates the offences in which police officers are victims in the Police Information System Saxony. In 2010, a total of 16 cases involving pyrotechnics were registered (out of 191 cases) [12], in 2011, incendiary devices/pyrotechnics were used in five out of 191 cases (2.2%), in 2012, 30 out of 307 cases (9.7%) [13]. The Bavarian State Ministry of the Interior, Building and Transport comes to similar statistics in the Bavarian Report on the Protection of the Constitution 2016 [14].

There are also some reports from various state police forces, including a report from the Berlin police from New Year’s Eve in 2015. During an operation, a female police officer was injured in the arm by pyrotechnic fire. The fireball, which was concentrated on one point of the clothing and had a temperature

of more than 1000 °C, destroyed the uniform. The flames penetrated not only the fire-retardant suit, but also the flame-retardant underwear. Thus, severe burns to the skin were caused [15].

In order to train how to deal with incendiary devices and pyrotechnics, the police of North Rhine-Westphalia, for example, offers special training measures. Here, police officers take part in realistic exercises that prepare them for situations such as the G20 summit in Hamburg, the opening of the European Central Bank in Frankfurt or football matches. For this purpose, the officers learn, for example, special deployment tactics, how to extinguish fires involving people and how to secure pyrotechnic objects. Fig. 2 shows that the police wear special protective shields and helmets to protect themselves from the flames and heat, among other things [16].

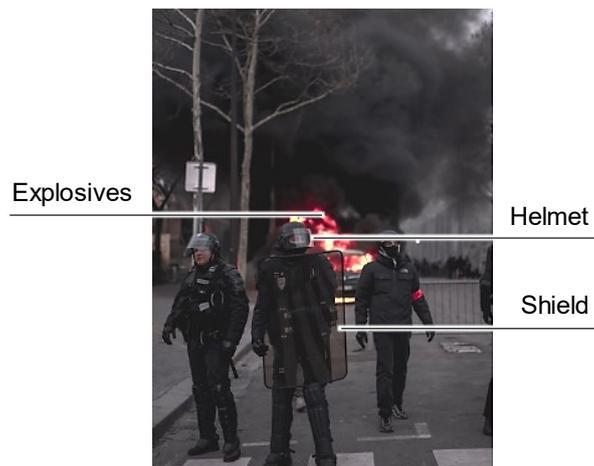


Fig. 2 Police forces with a protective shield and helmets canvas by Aloïs Moubax [17]

Protective equipment for emergency forces must meet a wide range of requirements, such as protection against impact as well as protection against heat and flame. The police officer's current protective clothing does not protect against Molotov cocktail attacks, as it shrinks and is destroyed by the heat generated [17]. The material from which the protective clothing is made is particularly decisive here. The equipment must be easy to wash and must be water-repellent as well as heat resistant. Also, hydrocarbons such as oil, petrol or diesel must be able to drain off [18].

To determine such a material, the project "Molotov cocktail protection – protective clothing material for emergency forces" is carried out. The project is funded by the German Federal Ministry for Economic Affairs and Energy and carried out by the Saxon Textile Research Institute e. V. (STFI), Germany and the Institut für Textiltechnik (ITA) of RWTH Aachen University, Germany. In several work steps, here called work packages, suitable blended yarns and fabric weaves are developed and tested in order to subsequently be able to make recommendations regarding technological as well as product-related aspects of protective equipment for emergency forces. The project will be completed in the end of 2022. Therefore, the results presented are preliminary and not all tests regarding the protective properties of the developed fabrics have been carried out yet.

2 Method

The project is divided into numerous work packages, which all have specific targets. The work packages that have been carried out are described in the following.

2.1 Development and production of suitable blended yarns as a prerequisite for reducing heat shrinkage

The aim of the first work package is to determine the yarn with the highest mechanical strength and the lowest tendency to shrink when exposed to heat or flame. For further investigations the yarn selection is being made after a comprehensive market overview has been compiled. A direct comparison between the different materials should allow an initial assessment of whether they are suitable for the desired use

and whether the requirements can be achieved as intended. In particular, the mechanical characteristic values are determined in order to be able to estimate the fabric requirements stipulated in the standard. These characteristic values are accordingly overlaid with the current status of fabric development for calculation.

2.2 Development and production of specially designed reinforcing fabrics

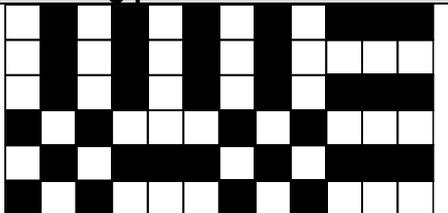
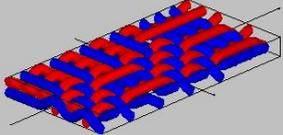
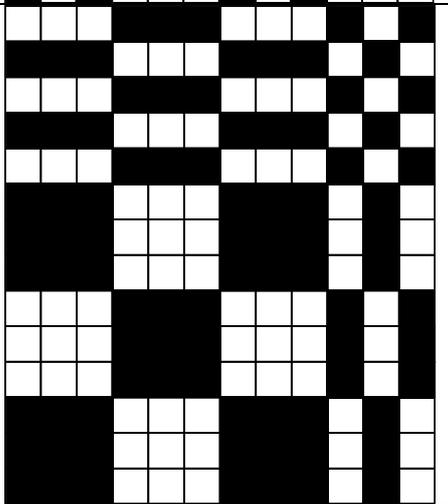
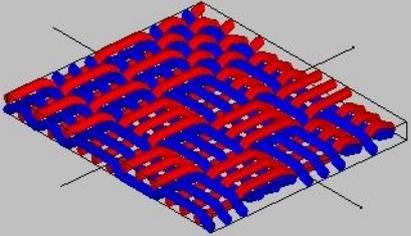
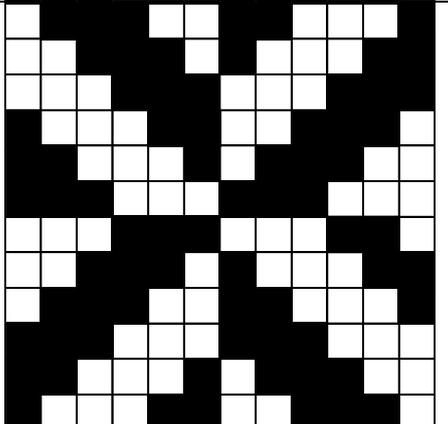
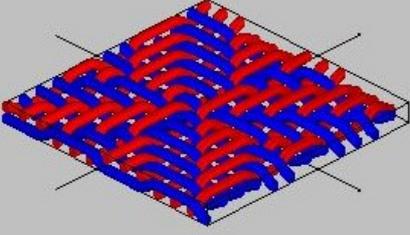
The usual fabric weaves are applied to an m-aramid yarn to check which one is most suitable. Standard weaves include:

- a) plain weave
- b) panama weave
- c) twill weave
- d) special weave

To determine the heat shrinkage, all fabric samples are clamped in a designed test rig in both warp and weft direction and heated up to a temperature of 1050-1150 °C.

After the trials with the standard weaves, new types of fabric weaves are developed: “interlocked rep”, “composite weave of rep, panama and canvas” and “openwork twill”, see Table 1.

Table 1. New types of fabric weaves (black: warp lift, white: warp lowering).

Name	Weaving pattern	3D-structure
Interlocked rep		
Composite weave of rep, panama and canvas		
Openwork twill		

For assessing the wearing comfort of the fabrics, the air permeabilities are being determined. First, the air permeability tests are carried out on the uncoated textiles in order to generally test the suitability of the new fabric weaves. The air permeability correlates with the heat retention capacity of the fabric. Air cushions form between the textile and the wearer's skin, which have an insulating effect. The air permeability of the three fabrics is tested in accordance with DIN EN ISO 9237 [19]. The tests are carried out under standard climatic conditions at 20.7 °C and a relative humidity of 66%. A differential pressure of 200 Pa is applied to the sealed sample and the air permeability is determined. For each fabric, a reference measurement is taken with a rubber plate to determine the leakage rate. This value is subtracted from the measured values to determine the actual air permeability.

Police officers are not only threatened with Molotov cocktails, but also with spikes and sharp objects such as knives. Furthermore, it is not uncommon for violent attacks to occur with the civilian population or demonstrators during a demonstration or a deployment of the riot police. The body protection equipment (KSA) can be damaged and ruptured in the event of this. It is not possible to change the KSA during an operation. In order to continue to provide protection for the police officers, the KSA must not tear. To assess the protective effect in terms of tear resistance, the tear propagation strength is considered. The tear strength requirements are at least 45 N across the warp direction and at least 45 N across the weft direction [20]. To determine the tear propagation strength, the leg tear propagation test is carried out in accordance with DIN EN ISO 13937 [21]. Each sample consists of two sets. These sets consist of 5 samples each in warp and weft direction. Samples with dimensions of 50 mm x 200 mm are taken from the fabrics. Two sets of 5 samples each are taken from each fabric. As only 0.6 m of the "openwork twill" could be woven out due to a shortage of material, only 4 samples are tested across the warp for these weaves. The tests take place under standard climate conditions at 20.7 °C and a relative humidity of 66%. In addition, burning tests are carried out according to DIN EN ISO 15025 [22].

2.3 Development of the equipment and the coating

A selection of possible finishes was investigated with chemical manufacturers. Water, oil and dirt repellency as well as excellent wash resistance and permanence played an important role. These finishes then are being applied as full bath impregnation in the padder process and subsequently condensed out. In another investigation, different polysiloxane coatings are combined with an oleophobic finish to prevent the adhesion of flammable substances. All functional samples are being examined and evaluated with regard to the burning test according DIN EN ISO 15025 as well as the 3M water/alcohol drop test and oil test according to AATCC 118:2013-00 [23,24].

In Table 2, the common scale of 3M water/alcohol drop test is shown. On a 5 cm x 5 cm fabric, three 5 mm drops are placed at a distance of 5 cm from each other. At an angle of 45°, the drops are observed for 10 seconds. If at least two drops have not penetrated into the fabric, three drops of the next higher level are applied to the fabric. This procedure shall be continued until one of the test liquids shows obvious wetting or wicking on the fabric under or around the drop within 10 seconds [25,26].

Table 2. Scale of 3M water/alcohol drop test [25–27]

3M Water Repellency Number	Composition of test liquid
W	Water
1	90/10 Water/Isopropanol
2	80/20 Water/Isopropanol
3	70/30 Water/Isopropanol
4	60/40 Water/Isopropanol
5	50/50 Water/Isopropanol
6	40/60 Water/Isopropanol
7	30/70 Water/Isopropanol
8	20/80 Water/Isopropanol
9	10/90 Water/Isopropanol
10	Isopropanol

In Table 3, the standard test liquids and their oil repellency numbers are shown. Starting with the test liquid with the lowest number (AATCC Oil Test Grade Liquid No. 1), small drops (approximately 5 mm) are applied to the test sample at five points along the textile. The drops are observed for (30 ± 2) s from an angle of approximately 45° . If there is no penetration or wetting of the fabric at the liquid-fabric interface and no wicking around the drops, drops of the next higher test liquid are placed on an adjacent area of the fabric. Again, the fabric is observed for (30 ± 2) s. This procedure shall be continued until one of the test liquids shows obvious wetting or wicking on the fabric under or around the drop within a duration of (30 ± 2) s [24].

Table 3. Standard test liquids [24]

AATCC Oil Repellency Grade Number	Composition
0	None (Fails Kaydol)
1	Kaydol
2	65:35 Kaydol:n-hexadecane by volume
3	n-hexadecane
4	n-tetradecane
5	n-codecane
6	n-cecane
7	n-octane
8	n-heptane

These tests are being carried out both in the unwashed and washed state. Therefore, all samples are subjected to the washing test in the non-commercial washing and drying procedure according to DIN EN ISO 6330 [28]. The samples are being washed 5 times at 60°C in the 6N + F procedure (including drying) and then tested.

The developed equipment is supposed to be wash resistant, hydrophobic and achieve a score of 10 in the 3M water/alcohol drop test and score of 5 in the oil test.

2.4 Development and modification of a test procedure

For the development of a test method which determines the burning behavior of fabrics for protective suits, the influence of the applied fuel quantity, the penetration capacity or adhesion capacity of the fuel as well as the fuel mixture are considered. Therefore, the so-called “technische Leistungsbeschreibungen von Körperschutzausrüstung” (short KSA), english “technical performance specifications of body protection equipment” of the police guideline of the state of North Rhine-Westphalia (NRW) is used. For this purpose, adhering substances and fire accelerants are additionally taken into account and the burning duration and damage are evaluated. For these tests, in accordance with DIN EN ISO 6530 “Protection against liquid chemicals”, the adhering substances and fire accelerants are applied to the textile in a trough. The weight of the sample before and after (absorption index) as well as the run-off quantity (rejection index) are being determined. In addition, the penetration (penetration index) of the fire accelerant is tested. This provides information on the effective fuel quantity and the repellency of the equipment and material combination. Subsequently, a burning test according to DIN EN ISO 15025 with 10 s surface ignition is carried out and the burning duration is determined [22]. Chemicals such as fuel oil, petrol and isooctane are used as fire accelerants and later combined with adhering substances such as coffee and glue.

For all work packages, most of the required data were either acquired independently through laboratory tests or taken from manufacturers’ data. Necessary assumptions were made by the experts of the participating research institutions.

3 Results

In the following, the results of the different work packages are discussed.

3.1 Development and production of suitable blended yarns as a prerequisite for reducing heat shrinkage

The yarn blends chosen are firstly Technora 50%, Kermel 28%, PBI 20%, Belltron 2% (hereafter referred to as Technora) and secondly Pyrotex 65%, Kermel 33%, Belltron 2% (hereafter referred to as Pyrotex). Based on the technical data, it could be assumed that both yarns fulfilled the required demands for the end product.

Table 4. Developed and produced blended yarns.

	Stretching	Elongation at break	Fineness related force	Maximum tensile force
Pyrotex	16.6 %	2216 cN·cm	13 cN/tex	424 cN
Technora	5.7 %	1899 cN·cm	53 cN/tex	1741 cN

Both developed fiber blends were processed into yarns, which were subsequently validated in weaving and fabric tests. It can be assumed that the acid resistance meets the requirements, as Technora, Kermel and PBI are aramid fibers. Both yarn structures consist of at least 33% of these fibers. Fiber blend 1 even contains 98% of them. Fiber blend 2 contains Pyrotex fibers, which belong to the acrylonitrile fibers, as its main component. According to the manufacturer, these have particularly high acid, base, UV, solvent, hydrolysis and oxidation resistance. In addition, the Limiting Oxygen Index (LOI) is 43% and it is antibacterial. The LOI is the “minimum volume fraction of oxygen in a mixture of oxygen and nitrogen, at 23 °C ± 2 °C, that just supports flaming combustion of a material under specified test conditions” [29]. Belltron is a polyester-based antistatic fiber. This has a negligible effect on the strength or fabric resistance with 2% fiber content.

3.2 Development and production of specially designed reinforcing fabrics

It can be seen that the area shrinkage is highest with the special and the twill weave with values between 59% and 80% (both in warp and weft direction). The warpage is similar, with the highest values of up to 65 mm for the twill weave. The plain and the panama weave show less shrinkage and warpage. The warpage of the two weaves is approximately the same and the area shrinkage is on average around 40-50% for both weaves.

The interlocked rep achieves the lowest air permeability with an average value of 582 mm/s. The interlocked weave is a mixture of a plain and rep weave, with high thread density and a panama weave with slight floatation. The result is a fabric with medium air permeability with an average value of 715 mm/s. The highest air permeability is achieved by the openwork twill with a mean value of 823 mm/s, see Fig. 3.

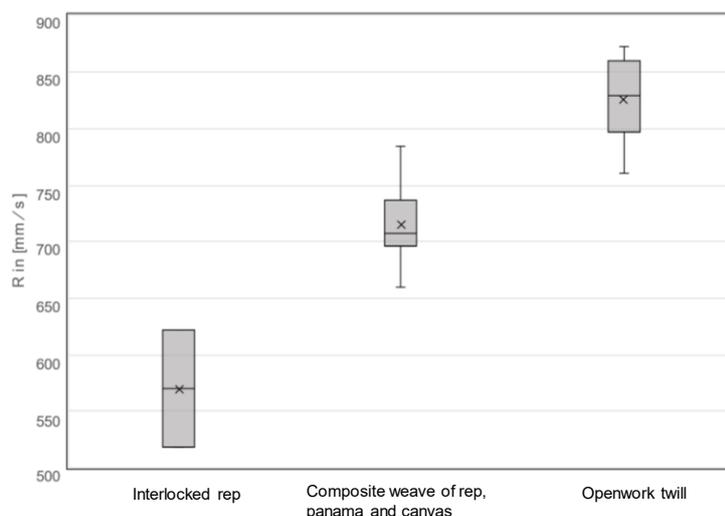


Fig. 3 Results of the air permeability tests.

The result shows that the air permeability of the different fabrics differs by up to 100 mm/s depending on the weave. The leakage rate is low at 2-4 mm/s for the composite weave and the openwork twill. The leakage rate of the interlocked rep is higher than that of the other two weaves at 12 mm/s. The standard deviations regarding the tear propagation force are low for all tests with values of 2-7 N. The difference in standard deviations across the warp and the weft, for the same type of weave, is insignificant. The interlocked rep achieves the highest tear strength (mean value across the warp 131 N and across the weft 107 N). The compound weave (mean value across the warp 122 N and across the weft 121 N) and the openwork twill (mean value in each case 78 N) have similar tear strength in both directions.

3.3 Development of the equipment and the coating

The examination of the finished coated functional samples has shown that all finishes achieve grade 10 (highest grade) in the unwashed state. When washed, a favored finish based on C6 also achieved a score of 10 in the 3M water/alcohol drop test.

For the oil test according AATCC 118:2013, the results varied greatly [24]. In the initial state (unwashed), the functional samples based on the C8 chemistry showed a grade of 6.5-4.5. Finishes based on the C6 chemistry achieved a grade of 4.5-5.5 in the best case. The worst finish was given a grade of 1.5. Without finishing, the grade was less than 1. In the washed state, the finishes lose 1-3 grade points depending on the substrate. Therefore, an optimization step regarding concentration and fixation was necessary.

3.4 Development and modification of a test procedure

The tests have shown that isooctane, as a short-chain hydrocarbon that penetrates well, is too volatile for use as a fire accelerant. 5 ml of this liquid already evaporated during application. The fire duration was a few seconds and was within the 10 s ignition time. A short flash fire of 1-2 s occurred with 10-15 ml isooctane. The amount of 5-15 ml petrol also showed no afterburning time. On contact with the burner flame, the accelerant burns off completely. Within 2-6 s during the flaming period, the flame extinguishes as the petrol is used up. Meanwhile, fuel oil led to afterburning times of 10-11 s, which was therefore later determined to be the fire accelerant. The experiments with additional coffee grounds showed that the fuel oil or petrol-coffee mixture burns longer. In this case, the coffee burns until the end and partially smolders. The fuel oil-coffee mixture of 10 ml/g achieves afterburning times of up to 41 s and afterglowing times of 19 s.

Further tests have shown that by increasing the organic components (coffee or glue), the burning time can still be greatly increased. However, this increase has a negative effect on the reproducibility of the test. Due to factors such as the organic substances falling off, the burning time is strongly influenced. Therefore, the following substances were used for the designed procedure:

- a) 10 ml of fuel oil and
- b) a fuel oil-coffee mixture of 10 ml of fuel oil and 1 g of coffee grounds

With these substances, the functional samples were tested raw, in the finished state as well as washed and unwashed. It was found that the finishing strongly reduces the penetration capacity as well as the absorption capacity. The lower the penetration and absorption capacity, the shorter the afterburning times. With the coating combination developed, it has been possible to achieve a run-off of the adhering fire accelerant from coffee and fuel oil during the burning process. Well-finished substrates can extinguish within 2 s afterburning time despite fire accelerant such as 10 ml fuel oil.

4 Conclusion

From the test results of the yarns, it can be concluded that both the Pyrotex and the Technora yarn are suitable for further processing as fabric. According to [20], a total fineness in warp direction of (29 ± 1) tex (Nm 35) and in the weft direction of (40 ± 1) tex (Nm 25) is required. The current fineness of the

weft and warp yarn is 33 tex due to a higher weave density for a smoother surface. Thus, there is the chance to adjust the parameters slightly, so that significantly better results are given.

Among other things, the tear strength is an important parameter for assessing the protective effect of the KSA with regard to its tear resistance. According to [20], the tear strength in warp and weft direction must be ≥ 45 N. The interlocked rep weave achieves the highest tear strength. The thread density is very high due to the interlocked rep weaves. The characteristic ribs form a tight weave with many closely spaced weave points. The visible difference in tear strength across the warp and across the weft is due to the different orientation of the ribs in the fabric. The composite weave of rep, panama and canvas as well as the openwork twill weave have almost the same tear strength in both directions. The reason for this is the symmetrical structure of the weave patterns. The composite weave of rep, panama and canvas consists partly of the plain weave and panama weave, which have the same properties in the warp and weft directions. In the openwork twill weave, the symmetry of the fabric results from the combination of the Z and S degrees, as well as the even distribution of the warp and weft threads.

All three fabrics produced exceed the required tear strength with values of 78-131 N and are therefore suitable for further processing regarding this parameter.

The air permeability is not only interesting for assessing the wearing comfort. In the event of contact with fire, the resulting air cushion provides additional protection against the flames. Compared to other media, air has a very low thermal conductivity coefficient of $0.024 \text{ W/m}\cdot\text{K}$ [30]. For this reason, air conducts heat very slowly. The air cushions act like a layer of insulation and prevent the heat of the flames from reaching the skin unhindered. This effect can prevent or at least minimize injuries caused by heat. To achieve this insulating effect, fabrics were made with weft reinforcement on the back of the fabric to create "air cushions" or "spacers" to the body. It can be seen from **Fehler! Verweisquelle konnte nicht gefunden werden.** that the ranges of air permeability values for all tests cover a range of approx. 110-120 mm/s. The interlocked rep achieves the lowest air permeability. The combination of the rep elements results in a high thread density with closely spaced weave points. This makes the fabric strong and has a higher air resistance. The composite weave of rep, panama and canvas is a mixture of a plain and rep weave with high thread density and a panama weave with slight floatation. The result is a fabric with medium air permeability. The highest air permeability is achieved with the openwork twill. The openwork twill weave has the lowest number of weave points as a combination of two twill weaves with Z and S degrees. The unbound thread length is not very long compared to the atlas weave. The uniform geometry of the Z- and S-grades creates large areas of unbound warp and weft threads, which increase air permeability.

Due to the good air permeability values, good wearing comfort can be ensured with all three fabrics.

5 Outlook

The developed fabrics have to be produced on an industrial scale. Afterwards the fabrics still have to be finished with the developed coating. The coating has a great influence on the air permeability. Therefore, the composite weave of rep, panama and canvas as well as the openwork twill are chosen for the following weaving tests. Both weaves are produced with the Technora yarn as well as with the Pyrotex yarn. The necessary tests which are described above are then carried out again. In addition to the air permeability test, the water vapor permeability test according DIN EN ISO 11092 is also carried out on the coated fabric [31]. The water permeability has a great impact on the wearing comfort of the KSA as a good perspiration transport is necessary [32]. A KSA is made up from the fabric with the best properties. For an industrial scale, the coating is done on the fabric itself and then made up to the final product. Here, an overall is planned for the police forces. According to the cooperation of the research institutes and police offices, the project results shall have immediate influence in the police PPE and daily life to decrease hurts of acts of violence with fire attacks.

Author Contributions

R. Krause: conceptualization, methodology, validation, formal analysis, investigation, resources, writing – original draft preparation, writing – review and editing; J. Kühn: conceptualization, methodology,

validation, formal analysis, investigation, resources, writing – original draft preparation, writing – review and editing; M. Gültner: conceptualization, methodology, validation, formal analysis, investigation, resources, writing – review and editing; Y. Dietzel: conceptualization, methodology, validation, formal analysis, investigation, resources; T. Gries: Supervision. All authors have read and agreed to the published version of the manuscript.

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