BIO BASED PRINTING WITH NATURAL DYES

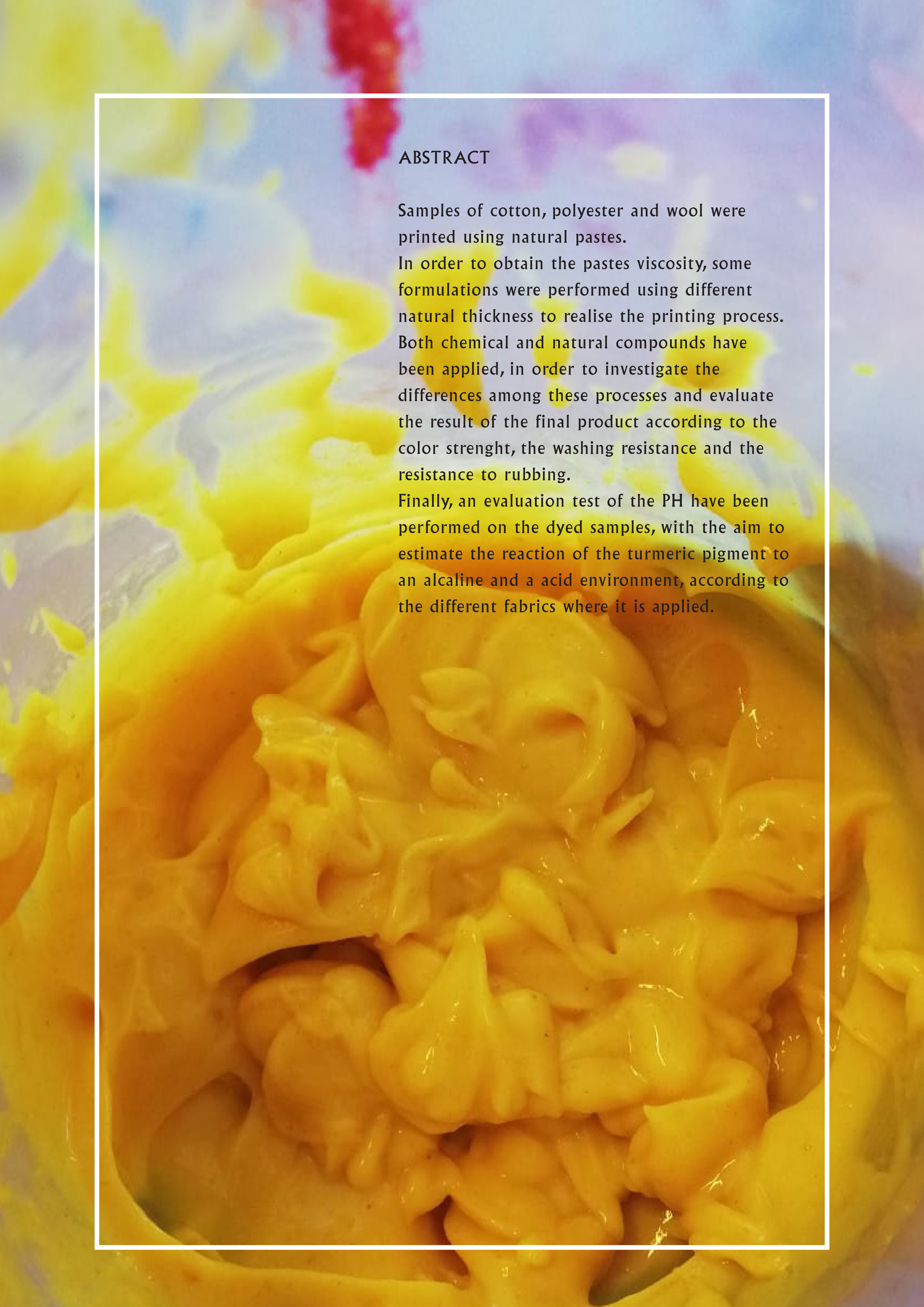
TRABAJO FIN DE MASTER

MASTER UNIVERSITARIO
EN INGENIERIA TEXTIL

Student: Sara Rondanini
Tutors: Eva Bou Belda,
Maria Angeles Bonet Aracil

July 2019

INDEX



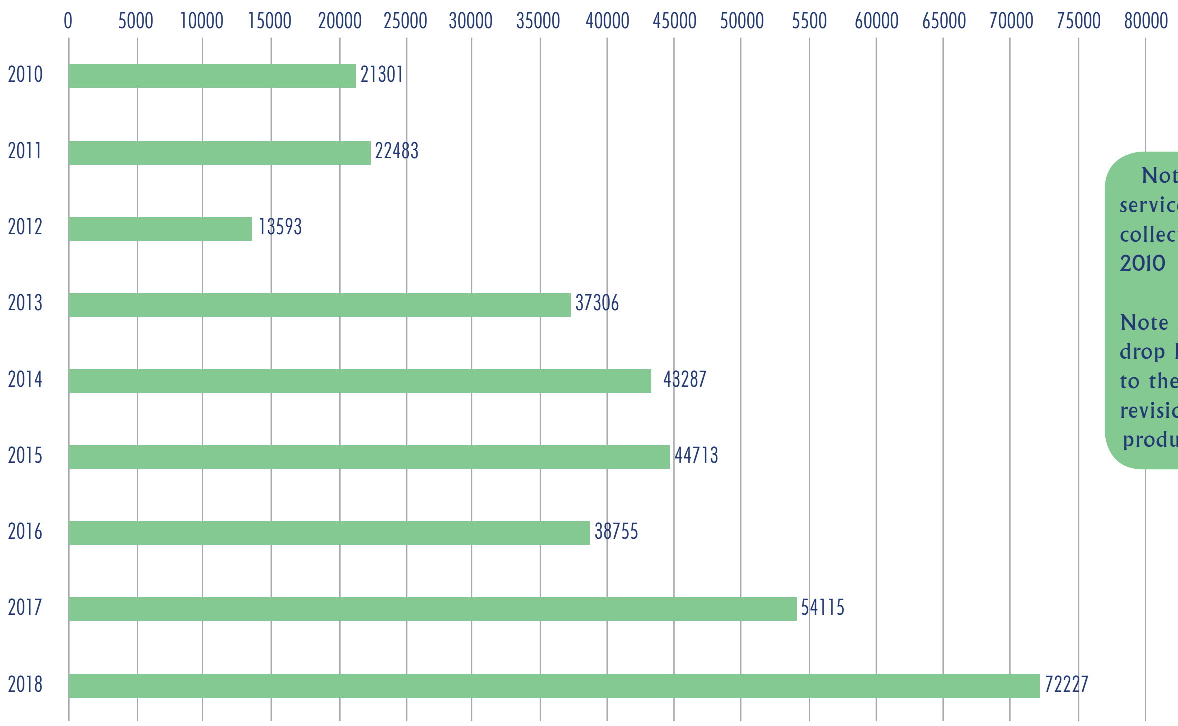
ABSTRACT

Samples of cotton, polyester and wool were printed using natural pastes.
In order to obtain the pastes viscosity, some formulations were performed using different natural thickness to realise the printing process.
Both chemical and natural compounds have been applied, in order to investigate the differences among these processes and evaluate the result of the final product according to the color strenght, the washing resistance and the resistance to rubbing.
Finally, an evaluation test of the PH have been performed on the dyed samples, with the aim to estimate the reaction of the turmeric pigment to an alcaline and a acid environment, according to the different fabrics where it is applied.

1. INTRODUCTION

For several years now, the textile production system has been strongly criticised for its role in the pollution of the environment.
To ensure the safety and traceability of raw materials and processes that are on the market and are used in the production of products, numerous initiatives have been developed, such as the Greenpeace Detox Campaign, promoted from 2011 to 2020, which involves 28 brands (including groups) and more than 50 suppliers. Again as ZDHC, in 2012, which includes 27 brands (including groups), 81 value chain affiliates and 17 associates.
There are also numerous Restricted Substances Lists (RSL), such as GreenScreen, Global Recycled Standard, Oeko-Tex, Bluedesign and Global Organic Textile Standards (GOTS), along with organizations such as Ecolabel and movements like Fashion Revolution.
All of these, along with others withe the same ideals, have helped to raise the awareness of the consumers, not only about consumption and emissions, but also about the harmful effects of many additives used during production (such as para-chloroaniline, metals, amine from azo dyes, carcinogenic dyes, allergenic dyes).
As a result, there has been a growing interest in everything that allows people to meet their needs in a more sustainable and less harmful way.
Fortunately, numbers are increasing: just consider the significant increase in the amount of services and products certified "Ecolabel" from 2010 to 2018, as well as the number of licenses that present this certification.

Evolution of the number of EU Ecolabel Products and Services from 2010-2018

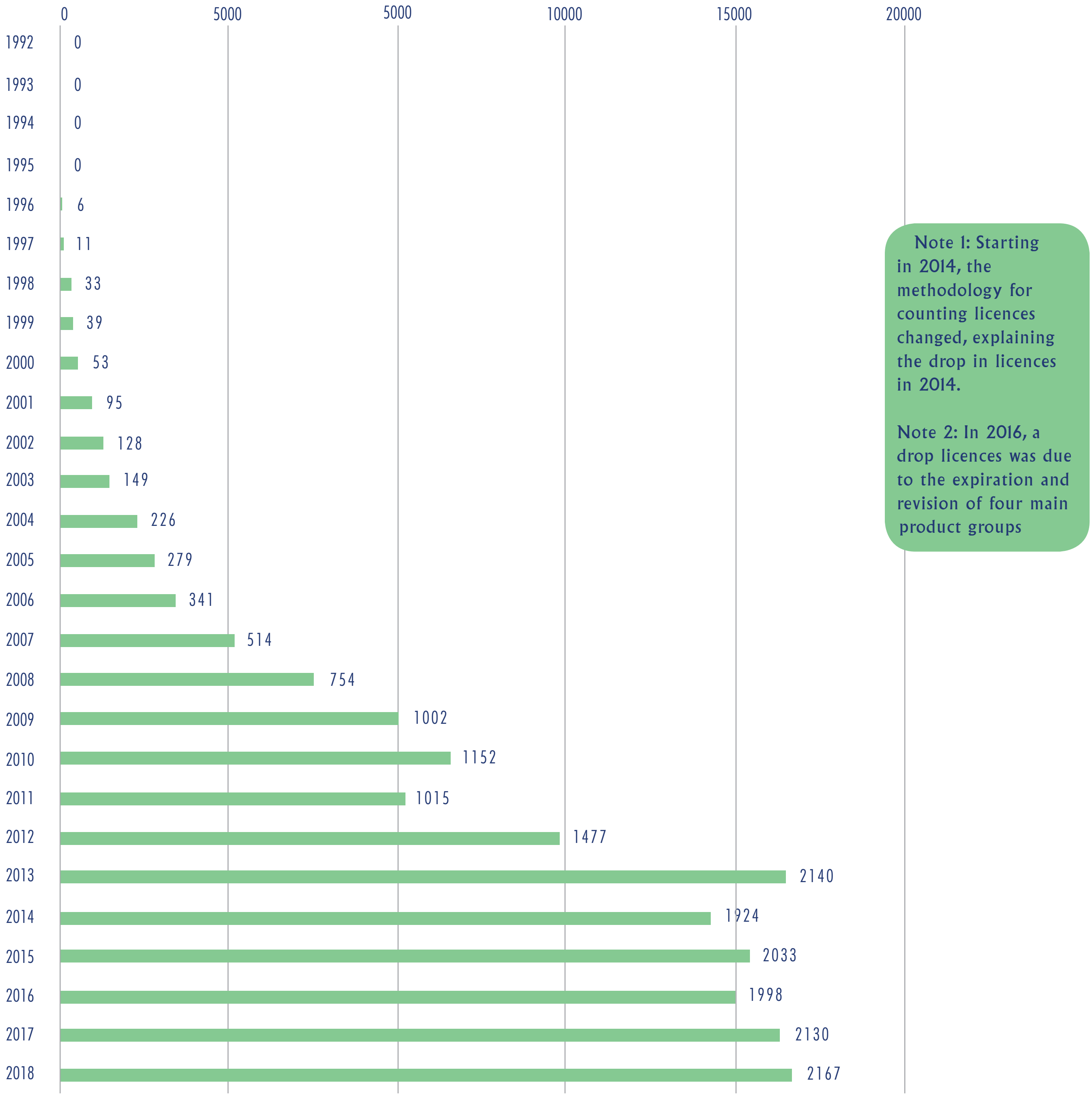


Note 1: Product/ service data was not collected prior to 2010

Note 2: In 2016, a drop licences was due to the expiration and revision of four main product groups

Source: ECAT - catálogo europeo de productos y servicios con Ecolabel (ec.europa.eu/ecat)

Evolution of the number of EU Ecolabel Licences from 1992-2018



Source: ECAT - catálogo europeo de productos y servicios con Ecolabel (ec.europa.eu/ecat)

Given all these factors, the textile world is strongly challenged to develop new production methods that encourage environmental sustainability and the health of the worker involved in the work and of the final consumer and this without forgetting the quality of the product.

In the following paper, particular attention will be dedicated to the quality of the product.

It will be focused expecially in the identification and the experimental verification of pigments, formulas and natural processes that can be considered as the best processes for the reproduction of prints on fabrics.

2.0 PRESENT NATURAL PRINTING INDUSTRY

In the process of making a print on a fabric, several steps that require many materials and substances are involved.
When the purpose is to create a pattern through the use of natural products, it is necessary to pay close attention, not only to the origin and method of extraction of the pigments that you intend to use, but also, for example, to the thickeners to be added to the paste for increasing the viscosity of the pastes and molding, to the stains to be applied for better color rendering on the fabric and to the final fixatives, designed to make the product durable.
In short, it is necessary to analyse in detail all those components that contribute to the success of the process.

2.1 Pigments

It is known that at the moment of the purchase, the color of the product is the first factor perceived by the buyer and, to date, not only by which shade characterizes it, but also how it has been placed and where it was originated.
For many centuries, the only pigments used had a natural origin. The processes of extraction and use were different but basically the dye was extracted from a vegetable, mineral or animal source.
Everything changed in 1856 following the accidental synthesis of mallow by William Henry Perkin and its subsequent marketing, which led to the development of synthetic dyes, which almost completely replaced the natural ones.
Despite the natural colorants have some limitations such as availability, color rendering and reproducibility of the shade, as can be seen from the table in Table 1[1], there is a considerable interest in the production of new vegetable pigments for textile applications, as these offer a safer dyeing alternative.
In fact, since they are obtained from renewable resources, they do not present health risks and even perform beneficial and curative functions and do not present disposal problems due to their biodegradability[2].
In fact, not only no chemical treatments are necessary in their preparation, but they can also be insect repellents, carry out UV protection and deodorization actions and have antimicrobial properties[3].
As a result, several research activities have been developed according the extraction of natural dyes, with the aim to increase the sources from which the pigment can be produced and the procedures for its processing and application.
In 2000, for example, a study was initiated at the RRL (CSIR), Jorhat, to extract dyes from sections of five different indigenous plant species in north-east India, such as Morinda angustifolia, Rubia cordifolia, Tectona grandis, Mimusops elengi and Terminalia arjuna.

Table 1. Some important colorants from industrial plants[1]

Plant	Family	Parts used	Pigment	Class	Colours obtained
Acacia Arabica	Fabaceae	Bark	Catecin, Epicatecin	Tannin	Yellow
Acacia cyanophylla	Fabaceae	Flower	Isosalipurposide	Chalcone	Yellow
Albizia lebbeck	Fabaceae	Bark	Quercetin	Flavonoid	Brick red
Allium cepa	Liliaceae	Dried skin	Quercetol	Flavonoid	Orange
Alkanna tinctoria	Boraginaceae	Root	Alkannin	Napthoquinone	Red
Acacia catechu	Mimosaceae	Wood	Catechin	Anthocyanin	Brown
Artocarpus heterophyllus	Moraceae	Wood	Morol	Flavonoid	Yellow
Adhatoda vasica	Acantaceae	Leaves	Vasicine	Alkaloid	Yellow
Berberis aristata	Berberidaceae	Bark	Berberine	Alkaloid	Yellow
Berberis vulgaris	Berberidaceae	Root/Bark	Berberine	Alkaloid	Yellowish
Butea monosperma	Fabaceae	Flower	Butryin, Isobutyrin	Flavonoid	Yellow, orange
Bixa orellana	Bixaceae	Seeds	Bixin	Carotenoid	Yellow
Caesalpinia sappan	Caesalpiniaceae	Wood	Braziline	Dihydropyran	Red
Carthamus tinctorius	Asteraceae	Flower	Carthamin	Benzoquinone	Yellow, red
Chlorophora tinctoria	Moraceae	Wood	Morin, Maclurin	Benzoquinone	Yellow
Coffea Arabica	Rubiaceae	Beans	Caffeine	Alkaloid	Brown
Crocus sativus	Iridaceae	Flower	Crocetin	Carotenoid	Yellow, orange
Curcuma longa	Zingiberaceae	Rhizome	Curcumin	Carotenoid	Yellow
Datisca cannabina	Datiscaceace	Leaves	Datiscetin	Flavonoid	Yellow
Eclipta alba	Asteraceae	Leaves	Wedelolactone	Coumarin	Brown
Eucalyptus	Myrtaceae	Leaves	Gallic acid, Quercetin	Tannin/Flavonoid	Yellow
Fraxinus excelsior	Oleaceae	Bark	Rutin, Quercitrin	Flavonoid	Yellow
Garcinia mangostana	Guttiferae	Fruit	Cyanidin-3-sophoroside	Cyanidin	Orange/brown
Haematoxylan compechianum	Leguminosae	Heartwood	Haematoxylin	Dihydropyran	Red
Isatis tinctoria	Brassicaeae	Leaves	Indigo	Indigoid	Blue
Indigofera tinctoria	Fabaceace	Leaves	Indirubin,Indican	Indigoid	Blue
Juglans regia	Juglandaceae	Bark	Juglone	Napthoquinone	Brown
Lawsonia inermis	Lytheraceae	Leaves	Lawsone	Napthoquinone	Orange
Lithospermum erythrorhizon	Boraginaceae	Roots	Shikonin	Napthoquinone	Red
Mahonia napaulensis	Berberidaceae	Bark	Berberine	Alkaloid	Greenish yellow
Mallotus philippinensis	Euphorbiaceae	Fruit	Rottlerin	Chalcone	Red/yellow
Melastoma malabathricum	Melastomataceae	Fruit	Casuraricitin,	Anthocyanin	Black
Mimosa tenuiflora	Fabaceae	Bark	Condensed tannins	Tannins	Purple
Mimusops elengi	Sapotaceae	Bark	Quercetin, Myricetin	Flavonoid	Brown
Morinda angustifolia	Rubiaceae	Roots	Morindone	Anthraquinone	Brown
Morinda citrifolia	Rubiaceae	Root	Morindone	Anthraquinone	Red
Myrica esculenta	Myricaceae	Bark	Myricetol	Flavonoid	Yellow
Nyctanthes arbortristis	Oleaceae	Flower	Nyctanthin	Caroteniod	Bright orange
Opuntia ficus-indica	Cactaceae	Fruit	Indicaxanthin	Betalain	Yellow, orange
Opuntia lasiacantha	Cactaceae	Fruit	–	Betalain	Yellow, orange
Pterocarpus santalinus	Fabaceae	Wood	Santalin	Flavonoid	Red
Punica granatum	Lythraceae	Fruit	Punicalgin	Tannin	Yellow
Polygonum tinctorium	Polygonaceae	Leaves	Indican	Indigoid	Blue
Quercus infectoria	Lythraceae	Rind	Gallic acid, Ellagic acid	Tannin	Yellowish
Reseda luteola	Resedaceae	Leaves/Seeds	Luteolin	Flanonoid	Yellow
Rheum emodi	Polygonaceae	Root	Rhein, Emodin	Anthraquinone	Yellow
Rhizoma coptidis	Ranumculaceae	Root	Berberine	Isoquinoline	Yellow
Rubia cordifolia	Rubiaceae	Root	Pupurin, Rubiacordone	Anthaquinone	Red
Rubia tinctorum	Rubiaceae	Root	Alizarin	Anthraquinone	Red
Saraca asoca	Caesalpinaceae	Bark	(+)-Catechin	Tannin	Brick red
Serratula tinctoria	Asteraceae	Leaves	Luteolin	Flavonoid	Yellow
Solidago Canadensis	Asteraceae	Plant	Quercetin, Quercitirin	Flavonoid	Golden yellow
Sophora japonica	Leguminosae	Seedpod/Flower	Rutin	Flavonoid	Yellow
Tabebuia avellanedae	Bignoniaceae	Heartwood	Lapachol	Napthoquinone	Yellow
Tagetes erecta	Asteraceae	Flower	Lutein	Carotenoid	Yellow
Terminalia arjuna	Combretaceae	Bark	Baicalein, Ellagic acid	Tannin	Light brown
Terminalia chebula	Combretaceae	Bark-Fruit	Chebulinic acid	Tannin	Pink, yellow
Tectona grandis	Verbenaceae	Leaves	Tectoquinone, Tectoleafquinone	Anthaquinone	Yellow

These were analysed and it was concluded that they can be considered as alternative sources to synthetic dyes for the dyeing of natural silk and cotton[4].
In the same year, the European Commission encouraged the project "Sustainable production of plant-derived Indigo", known as "SPINDIGO", which provided seeds and an agronomic plan for farmers; an identification of three different crops considered to be the best for different European regions; agricultural technologies for the extraction and purification of indigo; dyeing standards for the product and an environmental impact assessment. All with the aim to introduce indigo-producing crops into European agriculture, so as to obtain a long-term benefit in the rural and environmental sectors[5].
According to a study dated 2005, the numerous wastes coming from the food and beverage industry could be used as a source for the extraction of natural dyes for textile dyeing operations, in particular for the extraction of bright yellow and red colors from fruits and vegetables. Experiments have been carried out, for example, on pressed berries or grapes, distillation residues from liquor production, wastes and peels from the prcessing of plants and experimental dyes have been carried out on yarns of wool. The colour resistance, shade and solidity properties of the dyes were tested and the extracts were applied both as direct dyes and in the presence of iron or alum mordants. Finally, the results demonstrated the potential of this waste as a source for the natural extraction of dyes[6].
The table number 2[1] shows some of the pigments that have been extracted from the residues of the industrial processing of some plants.

Table 2. Wastes and by-products from different industries as sustainable sources of natural dyes[1]

Plant/crop	Type of product	Wastes as natural dye source
Grape	Wine	Pomace
Onion	Food	Peel
Red beet	Food	Peel
Black tea	Food	Extracted residue
Raspberries	Juice	Pomace
Black elder	Juice	Pomace
Sour cherries	Liquor	Distilled residue
Cherries	Strong liquor	Distilled residue
Blackcurrant	Juice	Pomace
Elder	Strong liquor	Distilled residue
Pomegranate	Food	Peel
Olive tree	Food	Waste water extract
Rosemary	Oil	Extracted residue
Rose	Oil	Extracted residue
Lavender	Oil	Extracted residue
Mate tea	Oil	Extracted residue
Saffron	Spice	Petal
Ash-tree	Timber	Bark
Teak	Timber	Leaves
Orange	Food	Peel

In the same way, investigations were also carried out into the dyeing potential of certain wastewater from industrial processes. In particular is worth mentioning the one of madder dyebath, that can be reused for wool dyeing. In fact, as shown by the analysis of the chromatic parameters and the solidity properties of the samples, the quality of the samples dyed in the reconstructed colour bath is the same of the one of the initial dyeing of the wool. In addition, an economic analysis has shown that the reuse of wastewater has saved 19.91% of the costs of dyeing wool with the robies[7]. Another study from 2012 showed that the wastewater produced by the olive oil extraction process can also be used as a possible dyebath for dyeing wool. It has been found that protein fibers have a high affinity with the aqueous extract of the olive mill wastewater, giving darker shades with generally good solidity, which can be jammed with the use of stains[8].

In this project, the pigments used to produce the print were extracted from the rubia tinctoria and turmeric plants, in order to obtain the two primary colours of red and yellow, respectively.

2.1.1 Focus on rubia tinctorium

//Description
The first dye used in the experiment that will be discussed later derives from rubia tinctorum, also known by the common name dyer's madder and described in detail by Dominique Cardon[9]. It is a light green herbaceous plant, with a system of long branched roots within which are concentrated numerous red dyes.

//Origin
Originally from the Middle East and the most eastern areas of Europe, the robbia has also been naturalized in some areas of central and southern Europe, as well as being introduced in the Far East (especially in China, Japan, Malaysia) and later in America (especially in the west coast of the United States, Mexico and South America).

//Parts of the plant used
The parts of the plant used to carry out the dyeing process are the roots, which in the Mediterranean area are also called alizars (from the Arabic ''al-'usara: succo'').

It was with this name that the roots of the robbia were traded from both the Levant and southern France and were sold preferably whole rather than in powder form.

//Dye composition

Blackburn[10] refers that dyer's madder biosynthesis typically results in compounds with sugar moieties attached (glycosides) and the same parent structure without sugar moieties (aglycons); glycoside derivatives have increased water solubility over their aglycon counterparts.
In 1826, Robiquet & Colin reported that Rubia tinctorum root contained two dyes, alizarin and purple, which fade more rapidly[11,12].
Subsequently, most nineteenth and twentieth century literature that followed similarly concluded that the main colorant present in the extracts of R. tinctorum was alizarin (CI 75330), traceable in the fresh roots of the plant.
Up to now it has been possible to extract thirty-six compounds from the roots of robbia, but alzarin certainly remains the most renowned.
The explanation for this reputation is partly given by the fact that of all the isolated compounds, only fifteen play an active role in the dyeing process, grouped within the Color Index (CI) as Natural Red 8.
The 2-O-linked disaccharide of alizarin, known as ruberitric acid, was first isolated from an unspecified species of rochleder in 1851[13], but it is only relatively recent that significant evidence has verified that ruberitric acid glycosides and glossy primeveroside are the components of primary anthraquinone in the roots of rubia tinctorum[14,15].
In fact, the total glycosides present in the roots of R. tinctorum are at least five times higher than the total glycosides, with individual concentrations of glycosides significantly higher than those of their counterparts.[16,15].
There is now sufficient evidence that alzarin and ruberythric acid, only occur in significant concentrations in rubia tinctorum.
Blackburn provides a list of the quantities of different components of the robbia traced.[1]
It reports that from the analysis of the plant it has been verified that another of the major compounds in planta is presented by Lucidin primeveroside[14, 15, 17, 18], but there are also amounts of Munjistin[18, 19, 20, 21], Galiosin (pseudopurpurin primeveroside)[19, 20, 22], Pseudopurpurin glucoside[19, 20], Pseudopurpurin[19,20,21,22,23,24], Rubiadin primeveroside[16, 22], 1 Hydroxy AQ[23], 1 Hydroxy 2 methyl AQ[18,24,25], Anthragallol[24], 2 Hydroxy AQ[24], 2 (Hydroxy methyl) AQ[24], Rubianine[26,27]. On the contrary, could be traced only very low amounts of Nordamnacanthal[17,18,19,20,28], Xanthopurpurin[17,18,19,20,24], Purpurin[15,17,18,19,20,21,22], Rubiadin[17,18,20,21] and trace amount of Lucidin[16,17,18,19,29].
Helmut schweppes showed the variety of colours that can be obtained if they are isolated from the roots of the dyer's madder and some of the colours mentioned above are used individually.

The range of colours varies from yellow to orange, from red to vermilion to crimson and even dark rust.
Dominique Cardon[9] reports that, if considered together, these dyes represent a value ranging from 2.3 to 4.4 % of the total weight of Rubia tinctorium roots.

//Harvesting
Harvesting takes place in autumn. In every country where it was grown, producers used to wait at least until the second year of growth of the plant before reaping it.
In France, for example, the roots were extracted after three years, while in Iran, after seven years, so that they provided a more concentrated amount of dye, which allowed to obtain a more intense crimson color, considered more valuable.
Recent studies have scientifically confirmed the validity of these practices, verifying that, in the first year of growth, the roots of the rubia contain only four of the many colorants found in the plant, although they contain a greater amount of alzarin in proportion to their weight than older plants.
What is important, in any case, is that the quantity of both the roots and the dye harvested increases significantly from the first to the third year of growth of the dyer's madder.
Other studies about this matter found that there is an increase from 340 kg/ha to 2760 kg/ha for dried roots and from 27.6 kg/ha to 195.1 kg/ha for dye[30,31].

2.1.2 Focus on turmeric

//Description
Turmeric is an evergreen plant, which reaches an average height of 1-1.5 m.
The rhizome forms a fleshy complex with a primary ellipsoid-shaped tuber that was once called "curcuma rutunda". Once ripe, it has numerous lateral, cylindrical and branched rhizomes called "curcuma longa".
The rhizomes are bright orange both inside and out, with a spicy odour when bruised.
The leaves, very large, elongated and lanceolate in shape, are dark green above and light green below, densely studded with pellucid spots.
The inflorescence is an up to 20 cm long spike, erect, which appears between the foliar cloaks. The flowers are placed in bracts, which open one at a time.
The fruit is never produced[32].

//Origin
Turmeric is thought to be originally from South Asia, most likely India, which is still the largest producer. Here, in fact, an average of 400,000 tons of turmeric is produced in a year, in an area of 130,000 hectares[33].
This plant can be grown in most tropical and subtropical areas, as long as the rainfall is adequate or suitable irrigation facilities are available.
Turmeric has been introduced in most tropical countries and has reached China, East Africa and West Africa since ancient times.
Although commercial production is currently concentrated mainly in India and southern Asia, Jamaica, haiti and peru are also important producers, while in Africa in many countries it is cultivated in gardens and sold in numerous markets.[32]

//Parts of the plant used
The rhizomes, fresh or dried and ground into powder.

//Dye composition
In the nineteenth century, for the first time, a yellow dye, at that time called curcumin, was isolated in the rhizomes of turmeric.
In reality, it is a mixture of compounds now collectively known as curcuminoids: curcumin, demethoxycurcumin and bisdemetoxycurcumin (CI 75300, natural yellow 3, natural dye E100 in the European Union)[9].
To date, at least 235 compounds have been identified within the plant, mainly phenolic and terpenoid compounds, including twenty-two diaryl heptanoids and diaryl pentanoids, eight phenylpropene and other phenolic compounds, sixty-eight monoterpenes, one hundred and nine sesquiterpenes, five diterpenes, three triterpenoids, four sterols, two alkaloids and fourteen other compounds.
However, Curcuminoids and essential oils are the main bioactive ingredients that show various bioactivities in vitro and in vivo.[34]
In the United States, this plant is generally recognized as safe (GRAS) by the FDA[35].
The curcuminoid content of turmeric rhizomes often varies according to varieties, locations, sources and growing conditions, while there are significant variations in the composition of essential oils of turmeric rhizomes with varieties and geographical locations. As an example, the yellow Madras turmericcontains no more than 3.5% curcuminoids while the Alleppey one presents a content of 4.5-6%, which is why it is more orange in colour.[36]
Furthermore, both curcuminoids and essential oils have a variable content depending on the extraction method and are unstable in the extraction and storage processes.
As a consequence, the quality of the commercial turmeric products can vary considerably.

//Harvesting
The turmeric is ready for collection 7-12 months after planting, when the underpart leaves turn yellow.
Harvesting is done by digging, being careful that the entire tuft is lifted together with the dry plant.

The over-leaf parts are cut, while the roots and adherent soil are removed and the rhizomes are washed out well.
In order to develop the well-known yellow colour and the distinctive aroma, the clean rhizomes undergo a cooking process in boiling water for one hour, under slightly alkaline conditions.
The resulting product is then dried in the sun for 6-8 days or in hot air dryers.
The average yield of fresh turmeric rhizomes is 17-23 t/ha when the crop is artificially irrigated, while it is generally 6,5-9 t/ha in naturally rainy growing areas.
In the case of Asian producers, exports represent only a small part of production (5% for India), as they are also large consumers, while non-Asian countries export the majority of their production.
International trade is estimated at 20,000 tons of dried rhizomes per year.[9, 33]

2.2 Thickeners

Thickeners are a fundamental step in the success of printing on fabrics. These agents are generally compounds with a high molecular weight whose task is to transfer to the fabrics the dyes and chemical compounds necessary to create the printing pattern, thanks to the plastic action that they give to the compound used.
As far as the environmental consequences of the use of thickeners are concerned, starting from the analysis of the wastewater of the processes, it has emerged that the use of biodegradable additives and guar rubber on the fabrics is preferable, since they are less harmful to the ecosystem[37].
The most recommended products to perform this function are therefore guar gum and its derivatives, alginates, methyl and carboxymethyl cellulose, xanthan gum and some exudate gums, because even with low concentrations of these products it is possible to obtain high levels of viscosity and have characteristics that facilitate the rheological behaviour of the compound[38].
In 2009, an investigation was carried out in which Amaranth (Rajgeera) was proposed as a thickener to be used in the textile printing of vat dyes as an alternative to wheat[39].
Prints made using these products as thickeners were then analyzed by measuring K/S and L*, a*, b* values by reflectance method, bending length, washing & rubbing fastness etc. and the results suggested that Amaranth (Rajgeera) can in effect be substituted for wheat in the production of prints on fabric.

In a similar way, in the same year a research was published regarding the use as thickener in textile printing of the starch obtained from germinated maize, generally considered as waste material and eliminated, which was compared with that extracted from ungerminated maize[40].
The prints, made with both products, were analyzed by measuring color value (K/S and L*, a*, b* value), bending length and fastness to washing and crocking.

The results obtained showed that germinated maize starch obtained from inedible maize could be used as a total or partial substitute for unsprouted or healthy maize starch.
Since wheat and corn are staple foods widely consumed worldwide, their replacement in textile processing will reduce the burden on their use as thickeners within this industry.
In addition, Alginate, carboxymethylated guar gum and carboxymethylated cellulose have been extracted from wastewater concentrates and printing paste residues and reused as thickeners in monoreactive dye pastes. Their performance was compared with that of the original polymers and studied through the rheological properties of the printing compounds and the parameters that determine the quality of the final result. The result showed that the quality of prints using recycled thickeners is comparable to those obtained with original thickeners[35,41].
In addition, there are several investigations that have been carried out with the aim to increase the characteristics of the gums as thickeners, through the formation of adducts with suitable vinyl monomers and by means of polymerization with free radicals.
By virtue of this, it is necessary to take into consideration some of those who have shown remarkable thickening properties regarding the production of pastes for textile printing. Examples include Abbas Polyacrylic Acid/British Rubber[42], polyacrylamide/guar gum[43], polyacrylic acid/arabic rubber or dextrin[44], polyacrylic acid/karaya gum and chewing gum with polyacrylic acid/ tamarind gum.[45]

2.3 Mordants

Natural dyes often require mordants, products that bind to the fibres of the fabric and at the same time are able to create chemical bonds with the pigments, preventing the fading of the colour and increasing the solidity of the dyed fabric.

There are three types of mordants: Metal salts or Metallic mordants, Tannins and Oil mordants. Unfortunately, many of the Metallic mordants are toxic and limited quantities can be used for the health of the consumer. [46]

To solve this problem, some mordants have been developed from natural plants, which do not represent a threat to the environment and the human health. They are considered harmless because they have a non-carcinogenic, non-toxic and biodegradable nature. If we additionally include the fact that they do not cause problems of pollution or wastewater disposal, it is clear that they represent a valid alternative to synthetic stains.[47]
Jamia Nagar, in her research "Perspective for natural product based agents derived from industrial plants in textile applications", offers a list of them: Eurya acuminate DC var euprista Karth[48], tannic acid[49], Rumex hymenosepolus root[50], Catechu an extract from the heart wood of Acacia catechu[51], Tamarindus indica L. seed coat tannin[52], Emblica officinalis G. dried fruit tannin[53], Terminalia chebula powder[54], and lemon juice[55].
The author also reports that more recent studies have found a useful application of Chlorophyll-a, extracted from plants, as a bio-mordant in the textile field and in particular in the case of wool yarns[56].
The study revealed that the K/S value of woollen fabrics that have undergone the dyeing treatment increases considerably as the concentration of Chlorophyll-a increases.
It was therefore demonstrated that the latter is able to improve the predisposition of the fabric to dyeing thanks to its Magnesium content, released in the presence of an acidic PH. It has also been verified that using Chlorophyll-a as a stain increases the fastness properties of woollen fabrics once dyed.

2.4 Natural dyes used as biosensors

The term "biosensor" was introduced by Cammann[57] , to desctibe all those analytical devices that covert a biological response into an electrical signal.
Biosensors par excellence must be highly specific, independent of physical parameters such as pH and temperature and must be reusable.[58]
The IUPAC 1999 recommendations state that a biosensor is an independently integrated receptor device capable of providing quantitative or semi-quantitative selective analytical information using a biological recognition element[59].

The purpose of a biosensor is in fact to provide rapid, real-time, precise and trustworthy information on the analyte of the interrogation.
The basic principle of a biosensor is to measure a biological recognition and transform it into another type of signal using a transducer.
The main purpose of the identification system is to provide the sensor with a high degree of selectivity for the analyte to be measured.

The interaction of the analyte with the bioreceptor is designed to produce an effect measured by the transducer, which converts the information into a measurable effect such as an electrical/optical signal[60].
Since the beginning of this century, an interest towards the use of senstitive dyes has risen.
In 2006, Solar cells sensitized with dyes (SDC) were assembled using natural dyes extracted from black rice, capsicum, variegated erythrin flowers, xanthine rose and algae as sensitizers.
The black rice extract obtained the best photosensitizing effect among the natural fruit extracts, leaves and flowers chosen, due to the better interaction between the carbonyl and hydroxyl groups of the anthocyanin molecule on the black rice extract and the surface of the porous TiO_2 film.
The conclusion was that because of the simple preparation technique, widely available and low cheap natural cost dye as an alternative sensitizer for dye-sensitized solar cell is promising[61].
In a similar way, in 2007, Wangcharee e others have developed color-sensitized solar cells (DSSCs) using natural colorants extracted from roses, blue peas and a mixture of extracts[62] Recently, in Sri Lanka, after electrical and electronic analysis of more than 100 natural colorants extracted from local plants such as fruits, leaves, flowers, stems, bark and roots, it has been observed that many of these colorants used that can be extracted from natural products, with a simple procedure can be used as photosensitizers for DSSC.

To evaluate the experiment were observed the values of short circuit current density, open circuit voltage and filling factor obtained for solar cells using photo anodes with Ti02 sensitized with different extracts of fruits and vegetables.
It was also observed that, in particular, Mangoostein extracts gave better results.[63]
More recently, an interest for the application of sensitive dyes in the textile field emerged[64] .
In 2015, Devarayan conduced a study regarding the Development of an eco-friendly, pH sensor based on electrospun cellulose nanofiber functionalized with a natural pigment extracted from red cabbage, obtaining a universal pH sensor capable of detecting pH values in the range of 1–14 by indicating the unique color code against each pH, stable at different temperatures and at prolonged time.

Moreover, the colors were reversible and the pH sensor was recyclable, which all together opens up new possibilities for using the developed universal pH sensor as a health monitor.[65]

In 2017, a textile-based optical pH sensors was produced using turmeric powder to dye cotton and polyamide 6,6 fabrics. Both fabrics showed a bright yellow color after dyeing and demonstrated color changes (towards red) when contacted with basic solutions. In this experiment, the pH sensing of the curcuma-dyed fabrics demonstrated an excellent fastness a proved color reversibility of the fabrics[66].
Regarding turmeric, it has been reported that this pigment can be applied on fabrics not only as a dye, but also as antifungal and antibacterial agent[67].
Moreover, the curcuma longa is known for its application as a PH-sensitive dye for sensors in contact with human skin thanks to its antioxidant, anti-inflammatory and wound healing biological activities.[68]

3.0 Purpose

Having seen and considered all the information previously collected, the main objective of this experimental research is to investigate processes, materials and formulas aimed at the production of natural prints on fabrics of different composition.
The aim of this project is to identify the best eco-sustainable methods for the realization of decorative motifs on cotton, wool and polyester, comparing them with their traditional synthetic counterparts in terms of colour fastness, resistance to washing and to dry and wet rubbing.

To achieve this result, the work was organised into several phases:

- Enquiry about the State of the art on natural printing processes and material supply;
- Experimental study of the formulas regarding the performance on the fabrics, up to the achievement of the suitable ones;
- Experimental study of the formulas identified in relation to different pigments (rubia tinctoria and curcuma)
- Production of prints with natural and synthetic formulas on fabrics for comparison;
- Analysis of the samples of each fabric with regard to colour fastness, rub resistance to wet and dry rubbing, washing resistance
- Focus on the study of curcuma and investigation of color behavior based on the PH environment

4.0 Experiment

This section will describe the materials and processes that led to the outcome of the project.
The components used in the survey to obtain the desired formulas will be described: both those that were subsequently abandoned and those on which it was decided to invest more time and research.
It will also explain the working processes investigated in an attempt to reach those that best reflect the objective.
In addition, the tests to which the dyed samples have been subjected will be presented, with the aim of verifying their solidity and resistance.
Finally, the results obtained will be analyzed in order to compare the performance of the different formulas and their output in relation to the composition of the fabric on which they were applied.

4.1 Materials

This section describes the various materials used according to the procedure that has been carried out

// Printing pastes
In the production of the printing paste, as far as that related to the traditional synthetic method is concerned, it was decided to use Lutexal provided by Archroma as main thickner, in association with resin.
For the natural counterparts, different components have been investigated: in particular chitosan with medium molecular weight supplied by Sigma Aldrich (in combination with acetic acid provided by Sigma Aldrich to allow the solution of the first), alginate equipped by Farmaquimica sur sl and gum arabic (later abandoned).

// Pigments
The pigments used were rubia tinctoria from Innovatec, with its characteristic red colour, and commercial turmeric in dust, which makes it possible to obtain yellow.

//Fabrics
The prints were made on plain fabrics with different compositions in cotton 210 g/m^2, wool 385 g/m^2 and polyester 148 g/m^2.

4.2 Methods

This section will show the experimental formulas encountered in the search for those finally used, along with the methods of extraction of the pigment and the printing processes that led to those ultimately employed.

//Developement of the formulas
As far as some components are concerned, during the research it was necessary to experiment with the formulation and application of different compounds before obtaining those that ensured adequate viscosity and performance.

In some cases, in fact, the formulations and the proportions of the components have been slightly and progressively variated, until a formula that appeared viscous enough to pass to the printing step was reached.
Then it was applied on the fabric following the printing method, but not always the final result was considered satisfying and in those cases the research on the compounds was restarted and so on, until a result that was evaluated as satisfying was reached.
Table 4 report a schematic summary of the formulations tested and those finally used.

Table 4. Formulas investigated in order to make the dye paste (the highlited are the final ones).

LUTEXAL	
#1	
30 gr/Kg	Lutexal
10 gr/Kg	Resin
1 L	Water
10 gr/Kg	Pigment

GUM ARABIC			
#1		**#2**	
200 g/Kg	Gum Arabic	400 g/Kg	Gum Arabic
1 L	Water	1 L	Water
10 gr/Kg	Pigment	10 gr/Kg	Pigment

ALGINATE			
#1		**#2**	
30 g/Kg	Alginate	40 g/Kg	Alginate
1 L	Water	1 L	Water
10 gr/Kg	Pigment	10 gr/Kg	Pigment

CHITOSAN									
#1		#2		#3		#4		**#5**	
20 g/ Kg	Chitosan	25 g/ Kg	Chitosan	40 g/ Kg	Chitosan	60 g/Kg	Chitosan	22 g/Kg	Chitosan
3 ml/L	Acetic Acid	6 ml/L	Acetic Acid	16 ml/L	Acetic Acid	10 ml/L	Acetic Acid	20 ml/L	Acetic Acid
1 L	Water	1 L	Water	1 L	Water	1 L	Water	1 L	Water
10 gr/Kg	Pigment	10 gr/Kg	Pigment	10 gr/Kg	Pigment	10 gr/Kg	Pigment	10 gr/Kg	Pigment

Observations about the developement of the formulas

The formula with Lutexal immediately proved to be effective, being the most traditional and non-experimental, offering the right viscosity of the paste and excellent printing performance.

The natural counterparts, of both an investigative and experimental nature, have been developed by adjusting and increasing basic and general formulas related to compounds made with the same components.

In the course of the experiment, the formula based on gum arabic was abandoned, as adequate results in terms of viscosity of the printing paste were achieved earlier in the case of alginate and chitosan, which provided a sufficient number of counterparts to compare with synthetic printing.

The most complex compound to be produced was the chitosan-based one.

Starting from a general recipe, it was modified by gradually increasing the dose of chitosan in order to increase the level of viscosity of the final mixture, so as to make the printing process possible.

In proportion to the quantity of chitosan, the amount of acetic acid has also been increased so as to allow the solution of the first, always starting from the volume indicated in the initial recipe.

Several tests have been carried out, which have led to an increase in the amount of chitosan in the compound of three times the initial one, always without obtaining the right viscosity and in this case in particular resulting in a too dense mixture.

At this point we decided to think instead about the quantity of acetic acid.

For this reason, once back to the initial formula, progressively higher concentrations of acetic acid were added, in conjunction with slight increases in chitosan, until the mixture obtained the right viscosity.

It was therefore found that the concentration of acetic acid is essential to give the right viscosity to the dye paste and not only to allow the solution of chitosan.

//Making of the Dyeing paste

During the experiment, several tests were carried out also in the case of the processes of extraction of the colour from the pigment.
The steps that make up this passage, in fact, have been progressively adjusted and improved, with the aim of making this part as performative as possible.
Table 5 shows synthetically and schematically the procedures experimented and the one adopted at the end of the process.

Note
The residues of the pigments in the first dyeing paste didn't effect the solidity of the final print, but the fact that the pigment didn't disperded perfectly in the initial solution brought to a lower concentration of dye in the compound and finally to a less vivid hue.
To obtain the best performance from the extraction process and avoid pigment waste, the second procedure has been developed.
Finally, with the aim of verifying the yield of the final print, the third process of composition of the dyeing paste was also developed, but since the final output of this one did not differ significantly from the previous one (#2), it was decided to consider the second process as valid.

Tab 5. Processes investigated in order to make the dye paste (the highlited is the final one).

MAKING OF THE DYEING PASTE			
Process	#1	**#2**	#3
Pigment extraction	The pigment was mixed with the water at room temperature.	The pigment was solved into hot water.	The pigment was solved into hot water.
Mixture making	To make the dyeing paste, the obtained solution was mixed in the compound with the other components	To make the dyeing paste, the obtained solution was let to cool down and then mixed in the compound with the other components	To make the dyeing paste, the obtained solution was let to cool down and then filtered to remove any residual particle
Examination	In the final paste were still visible pigment residues, since the material didn't solve perfeclty in the room temperature water.	The final mixture still had some impurities, but these were almost imperceptible to the eye	The final paste didn't show visible contaminations due to resudues.

// Print machine

For the mechanical realization of the print, a hand flat screen printer was used.
The technique used was direct application, to say the dye paste has been directly applied to the fabric.

//Making of the print

The dyeing compound was applied to all fabrics at the same time.
Wool, cotton and polyester were in fact arranged in different quadrants under the mesh of the hand flat screen printer and the fresh printing paste was passed on it four consecutives times.
Then the fabrics were let to dry in the dryer machine dry at 110 °C.

4.2.1 Pretreatment with chitosan

Sample fabrics of cotton, polyester and wool were pretreated with a medium molecular weight (5 g/L) chitosan solution applied by foulard treatment.
In addition, three samples of cotton, polyester and wool were taken as counterparts and did not receive any previous treatment.
Subsequently, the printing paste with alginate and turmeric was applied to each cotton, wool and polyester sample, both pretreated with chitosan and not.

4.2.2 Colour measurament

The determination of samples' colour was carried out by the following standard procedure. The equipment Minolta CM-3600d UV-visible spectrophotometer used as a illuminant D65/10° observer, in terms of CIELAB values (L*, a*, b*) and colour strength (K/S).

The relative colour strength (in terms of K/S value) of different natural dyed cotton fabrics was measured by the light reflectance technique using the Kubelka–Munk equation.

K/S= (1 - R)2/2R (1)

where K is the coefficient of absorption; S is the coefficient of scattering and R is the reflectance.

Total colour difference of dyed cotton samples were obtained using following relationships:

Colour difference (E)= [(L)2+(a)2+(b)2]1/2

4.2.3 Fastness analysis of the prints

This paragraph will deal with the stage related to the different quality analyses carried out afterwards on the samples, concerning each fabric examined and each formula used to make the prints' standard.
Further than the color measurement, a rubbing fastness test has been performed following the regulation UNE-EN ISO 105-X12:2016 and a washing test was carried out in accordance with UNE-EN ISO 105-C10:2006 procedure A1S using multifiber fabric "SDC multifibre DW" standard: BS EN ISO 105 F10.

4.2.4 Halochromic effect

Given the results of the previous chitosan pretreatment process followed by printing with alginate, compared with untreated fabrics on which only the printing compound was applied, a test was subsequently performed to verify the reaction of the pigment of the turmeric in basic or acid environments.
To carry out the current test, the samples of each fabric on which all the formulas examined during the experiment were used were taken into consideration.
To each of them were then applied an alkaline solution (with pH 9) on the left margin and an acid (with pH 4) solution on the right margin.

5. Results

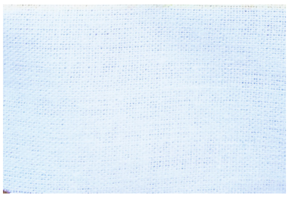
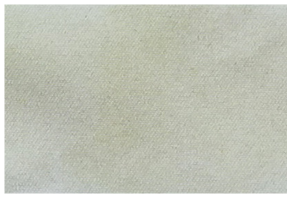
This section will show the results obtained from the named methods and the observations and analysis about them.

5.1 Printed samples

Once the printing mixes were applied, it was possible to notice differences in the final result.
These depend not only on the formula used to make the diverse compounds, but also on the composition of the fabrics on which they were applied.
In fact each paste created a different bond or reaction depending on the textile with which it was in contact, leading to various results visible even to the naked eye, which were then measured compared thanks to the tests mentioned above.

5.2 Color measurement

Printed fabrics comparison table

	Cotton	Wool	Polyester
Plain fabric			
Lutexal			
Chitosan			
Alginate			
Chitosan pretreatment + alginate			

Observations about the printed samples

Looking at the dyed samples, it is immediately visible that in all cases there has been a change of colour in the final product with respect to the initial fabric.

The most intense colour can be observed in the case of printing with Lutexal, while coating with the mixture containing chitosan is the least effective from the point of view of the intensity of the colour, especially when applied to polyester.

At the same time, the use of this product as a pre-treatment on which to apply the mixture containing alginate allows to obtain a good outcome and increase the performance of chitosan.

Even the use of the alginate compound alone allows to obtain a positive result, even if the printing with this product applied on polyester leads, as in the case of chitosan, to a more faded hue.

Analysing the results from the point of view of the fabrics, it can be seen that the case of wool is the one that allows a better grip of the tint, while polyester is the one that leads to a weaker performance, especially in the case of natural mixtures.
At the same time, cotton, more and more evident in relation to natural pastes, allows to obtain a less full colour compared to that obtained by the application on wool, but sufficiently bright, except for the already mentioned case of printing containing chitosan.

After the printing process, each fabric was subjected to a spectrometric test, based on the chromatic coordinates L*, a*, b* ant to the value DE*ab.
By comparing the initial colour of the each plain fabrics with that of its corresponding printed, the colour grip was analysed, in order to investigate the dyeing power of each mixture used.
This analysis was in fact based in particular on the data offered by the parameters that indicate the color difference between the undyed fabric and the same one after the application of the pigment, considering the color difference (DE*ab), the lightness L* of the color (L*=0 refers to black and L*=100 refers to white) and expecially the value of the parameter b* (-b* refers to blue and +b* refers to yellow).
Tables 6-7-8 show the values obtained from the spectophotometer test on the samples.

Tab. 6. Color values and difference of hue of printed cotton

	L*	a*	b*	DE*ab
Cotton	83,0608	1,4941	-5,65	
Co Alginate	79,6175	-4,7419	38,8658	45,0822
Co Chitosan+alginate	81,2545	-5,0806	43,3593	49,4813
Co Lutexal	81,9578	-9,4677	65,4085	71,9075
Co Chitosan	80,8688	-5,4015	29,4003	35,7894

In the case of cotton, it can be stated that all cases of printed fabrics are traceable within the yellow area, given the high b* values.
A slight green tinge was also identified by the slightly negative a* values.
In this case, in particular, all the most extreme values were recorded for the sample on which the synthetic paste was used.
The L* value in fact shows that the Lutexal sample is slightly lighter than the other ones, while the b* and DE*ab values demonstrate that this is at the same time the fabric printed with the most intense yellow colour.
On the contrary, the chitosan-based print is the most faded one, with the lowest b* level, while it is possible to notice an improvement in the performance of this product and of the alginate formula and an increase in the final values relative to the use of the alginate paste, in the event that this is applied to the fabric after a pre-treatment of the latter with chitosan.

Tab. 7. Color values and and difference of hue of printed polyester

	L*	a*	b*	DE*ab
Polyester	85,8987	-0,2265	-0,0582	
Pes Chitosan+alginate	81,198	-4,6266	30,573	31,3006
Pes Chitosan	83,3033	-1,2703	17,7861	18,0622
Pes Lutexal	79,2759	-12,7278	57,6752	59,4414
Pes Alginate	78,1835	1,0944	28,9141	30,0111

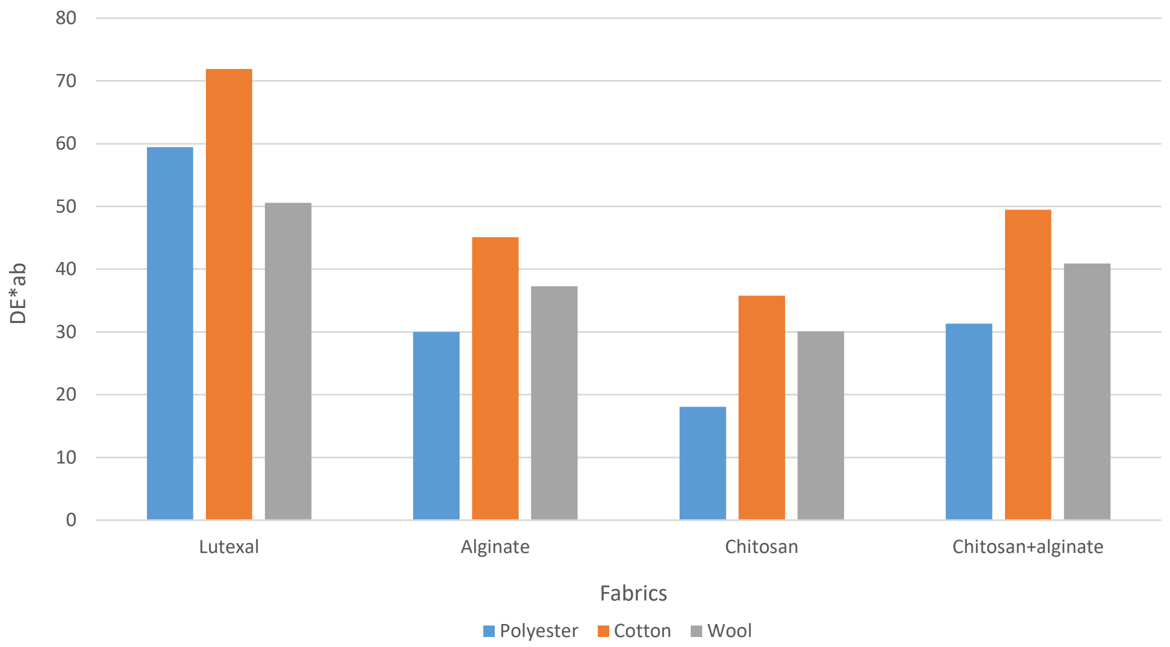
Regarding to printing on polyester, as in the previous one related to cotton, it is possible to determine that in all the cases the color can be traced in the yellow area, even if the second hues detected are the green (-a*/b*) when the fabric has been moulded with alginate (after a chitosan pretreatment), chitosan and lutexal, while the application of the alginate paste on this has led to an identifiable red (a*/b*) shade.
It is also possible to affirm that even in this case the chitosan-based print proves to be the softest as a result of the hue, showing the lowest b* value.
In addiction to that, the colour obtained from the application of the chitosan paste is the lightest too, given the higher L* level compared to other cases.
This can also be seen from the DE*ab data, which show a lower difference of color value in the case of this compound.
On the contrary, the Lutexal print proves to be the one with the highest differnce of color also in this case, as in the previous one regarding the cotton fabric, while the best performance among the natural compounds is given by the alginate paste on chitosan-pretreatd fabric.

Tab. 8. Color values and and difference of hue of printed wool

	L*	a*	b*	DE*ab
Wool	84,6165	-0,0544	19,1239	
Wo chitosan+alginate	78,0663	0,2783	59,5155	40,9206
Wo lutexal	79,1884	-2,5585	69,3532	50,5838
Wo alginate	77,411	1,0815	55,6615	37,2586
Wo Chitosan	79,5294	-2,4106	48,6721	30,0754

In the case of printing on wool, as in the previous ones, the positive and high values of b* make it possible to trace the colour in the yellow area in all the samples processed. The application of pastes with Lutexal and chitosan also makes it possible to identify light colours in the green range (-a*/b*), while the colour resulting from the use of the alginate compound can be traced in the red spectrum (a*/b*).
As far as DE*ab values are concerned, they all show a change in colour in the fabric following the application of the print, particularly in the case of Lutexal, immediately followed by the compound with alginate on pre-treated fabric.
At the same time, the print made with chitosan alone is also the lightest, since it has the highest L* rating and the softest, with the lowest DE*ab marking.
Nevertheless, the performance of chitosan improves considerably when it is used as a pre-treatment on the fabric, followed by the application of the printing formula containing alginate.

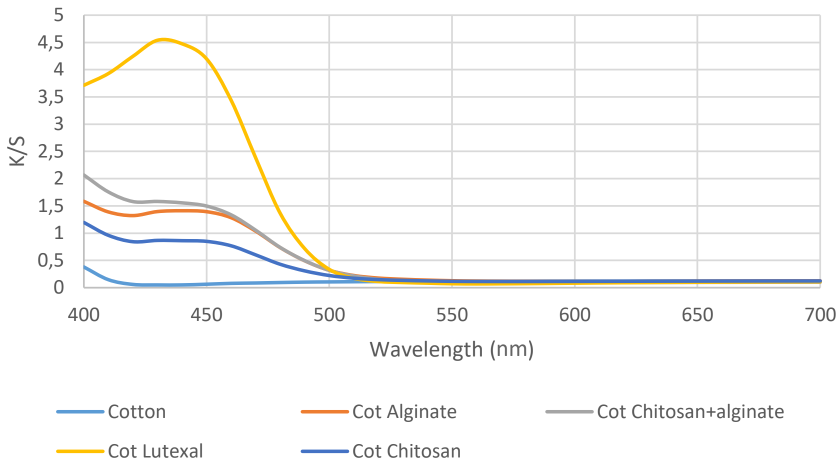
Comparison of the color results depending on the fabric



As shown in the graph, taking DE*ab values into consideration, the fabric that offers the best performance in terms of intensity is cotton, especially when printed with lutexal or alginate after having undergone chitosan pre-treatment.
This is probably due not only to the natural composition of the cotton under examination, which allows the natural dye to cling more easily than in the case of a synthetic fabric, but also to the thickness of its texture, which is impregnated with printing with considerable ease, being a fabric with a medium-light hand.
Very good results are also obtained from wool, especially when it undergoes the application of the alginate compound, after having been pretreated with chitosan.
Unlike the previous cases, polyester has the lowest levels of colour difference, especially when it comes to the performance of ecological compounds.
Also in this case, a reason can be found in the composition of this fabric ,that being synthetic, allows the color to grip with more difficulty, especially when it is made with natural raw materials.

In addition to the prior verifications, an examination was also performed that took into account the parameter of the color strength (K/S), to test the quality measurement of each sample in terms of depth of the color dyed fabric, as shown in tables 9-10-11.

Tab. 9 Color strenght wave related to cotton

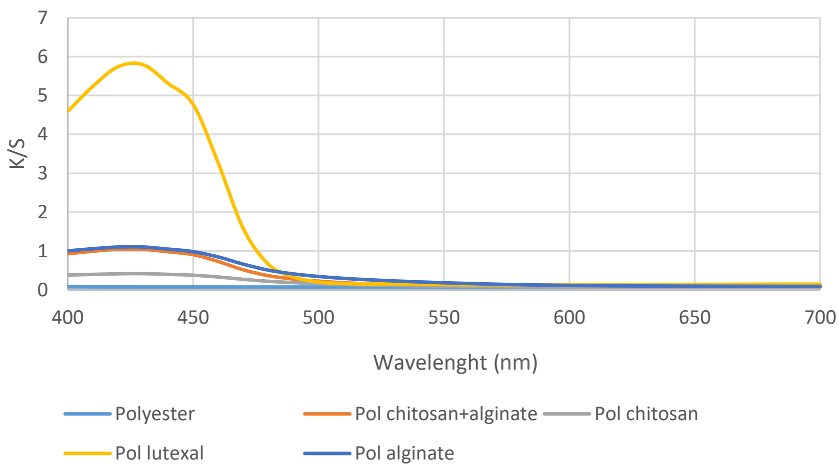


As shown in the figure, the highest levels of all the curves represented are in the first part of the graph, between 400 and 450 nm.

This allows to ulteriorly verify that the area of color within which the prints, realized with any formula on cotton, can be identified, turns out to be the one of the yellow.

The synthetic formula shows that it has a more intense colour than its natural counterparts, in particular compared to the one containing chitosan, which is the most faded.

Tab. 10 Color strenght wave related to polyester

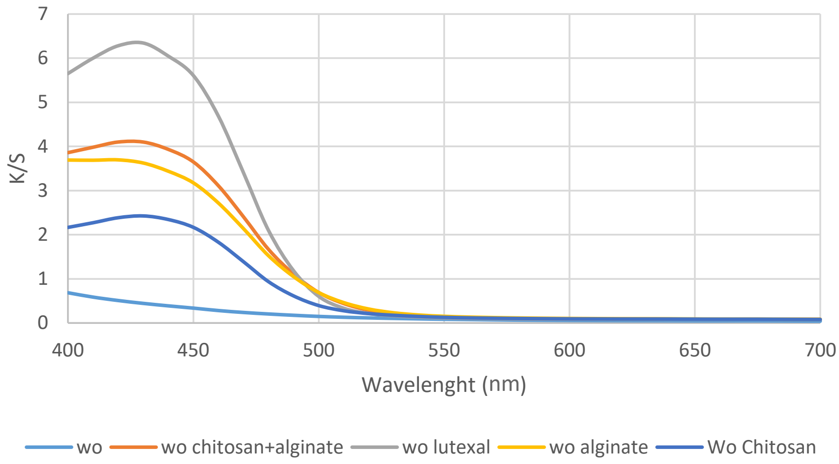


The curve in the figure shows that there has been a colour change in the yellow area in polyester due to the application of the compounds.

This is especially visible in the case of printing paste containing Lutexal, while natural pulps remain at a lower level, especially the one containing chitosan, which is the least performing.

This is probably due to the synthetic nature of the fabric, which is more reluctant to apply organic compounds.

Tab. 11 Color strenght wave related to wool



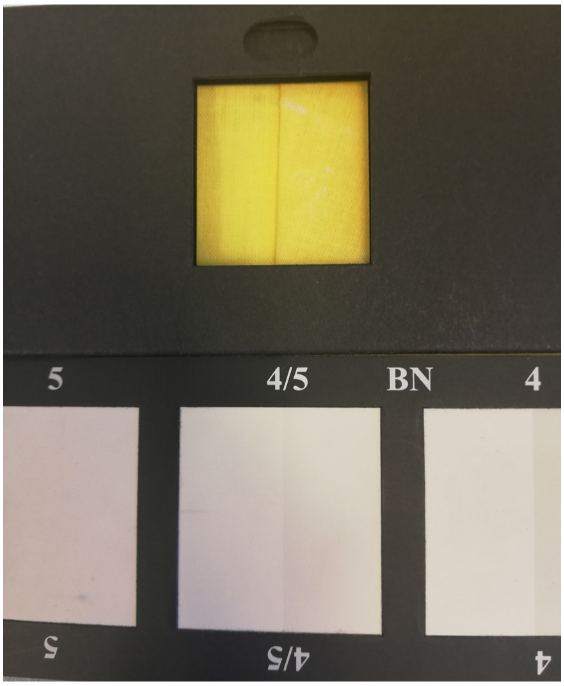
As in the other cases, also for wool it is possible to verify further the change of colour of the fabric after the application of the prints.
Also in this case, the Lutexal-based mixture proves to be the most performing, while the chitosan-based one is the least successful, although it proves to be more performing than in the previous cases concerning cotton and polyester.
An excellent result is also visible with regard to the other two natural mixtures: the alginate applied alone and on fabric pretreated with chitosan, in fact, have a rather high curve in the area of yellow, which shows their effectiveness.

Observations about the spectrometric test:
Analyzing the graphics and considering the values of the variable b*, which is always positive, these verify in any case the change in colour of the fabric under examination. This is further confirmed by the trend of the colour resistance curves, which allow us to observe that these are higher between the values 400-450 nm.
Thanks to this verification, it can be stated that the different printing mixtures with turmeric used during the experiment have produced a colour variation in the range of yellow on the fabrics to be printed.
As shown in the figure below by the DE*ab values, Lutexal paste is generally the one that offers the greatest colour difference between the initial solid colour fabric and the final print.
While the application of the printing paste using chitosan as a thickness is the least effective in terms of colour resistance, the use of this product as a preparatory treatment for the fabrics leads to very good performance when followed by the application of the printing paste that contains alginate.
At the same time, in the case of the single use of the compound of alginate as a printing thickner, the values relating to the setting of the color are not much lower than its use combined with chitosan.
As far as fabrics are concerned, those of natural composition, namely cotton and wool, are the most performing in terms of printing reception, since in these cases the highest

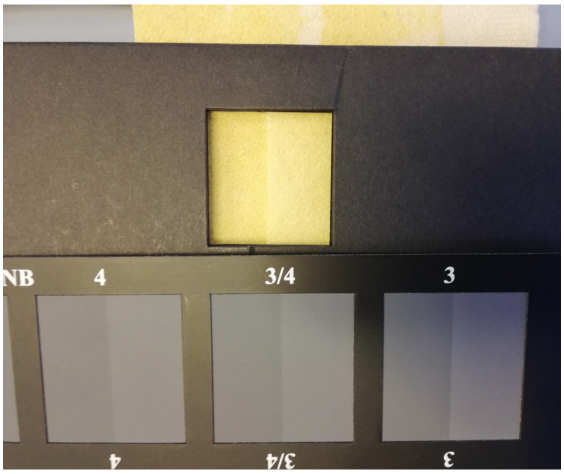
values are found with regard to the intensity of the colour and the variation in the shade of the fabric.
On the other hand the synthetic fabric, although registering variations in the intensity of the color after the printing process with all the mixtures, is the least favourable in general for the application of natural compounds, while mantains the average results with regard to the performance of the synthetic paste.

5.3 Color fastness

The printed fabric samples were tested to assess the resistance of the tint to washing and rubbing treatments, in order to measure the level of colour dispersion and the level of degradation of the print on the treated part.
The samples in exam, after being subjected to the fastness analysis, were compared with the corresponding counterparts who did not undergo the treatments described above.
The difference between the colour of the print before and after the named process was in fact quantified with special measuring instruments, with the aim of evaluating the performance of the various prints realized and, consequently, of the different compounds used.



white scale used to measure the descharge

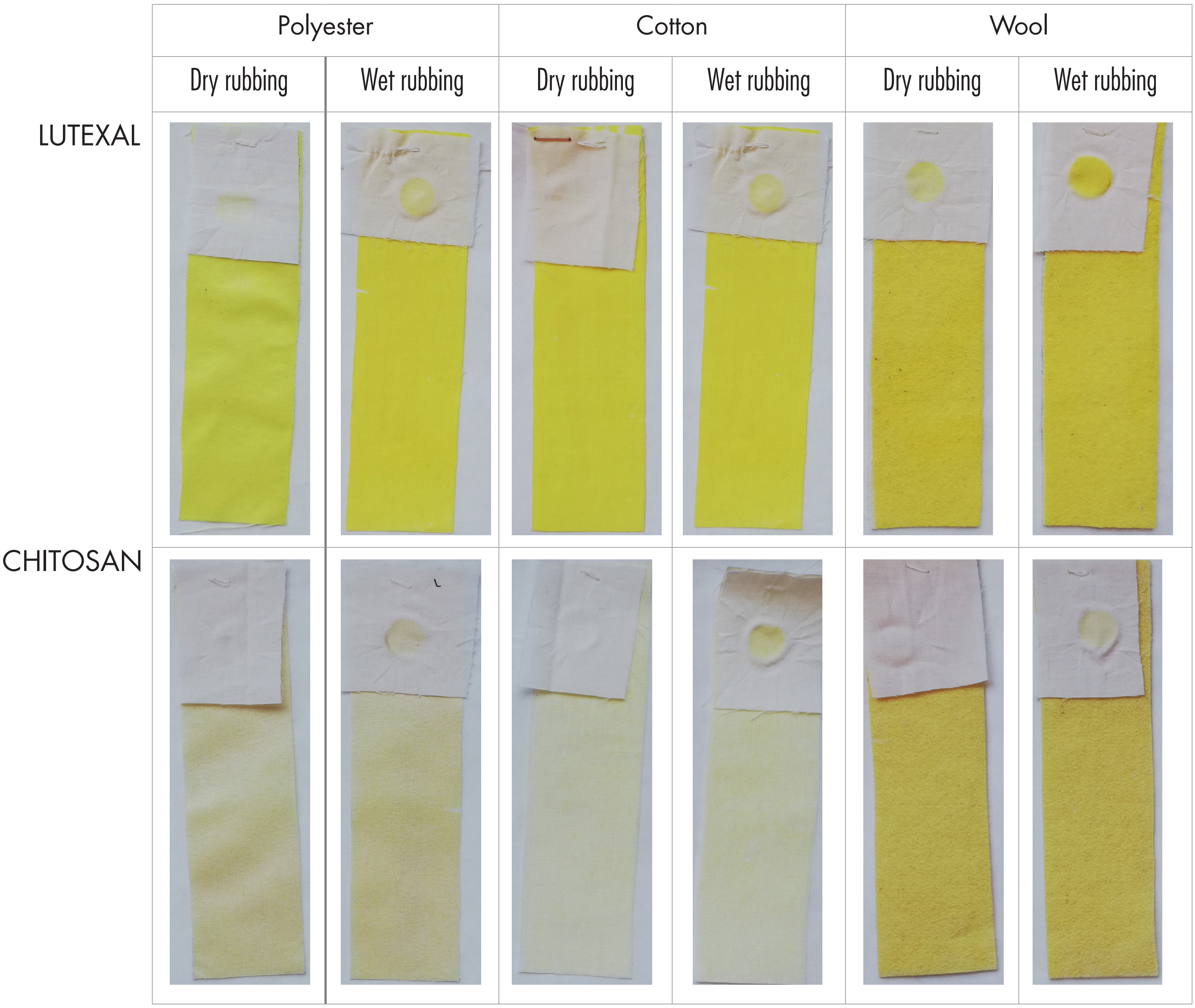


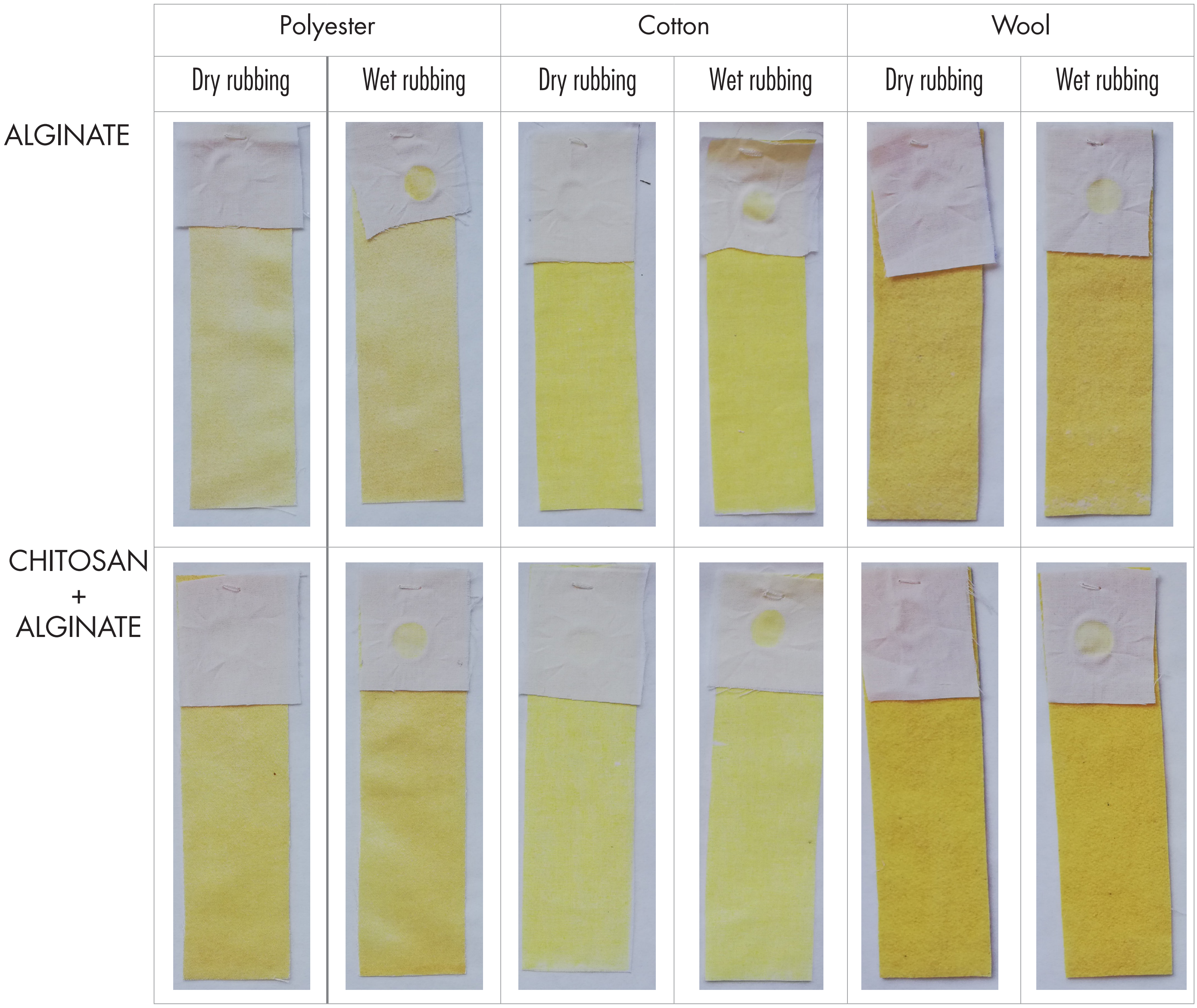
grey scale used to measure the degradation

5.3.1 Rubbing fastness

The analysis in question, also known as the ‘crooking test’, consists of transferring the colour from one fabric (in this case the printed sample) to another white test fabric, which can be either dry or moist.
The more colour is transferred, the more the fabric “crocks”.
The purpose of this test is to determine the amount of discoloration transferred from the surface of the coloured textile material to other fabric by rubbing.
The measured values are those of degradation of the hue of the print on the sample and that of discharge of the colour on the white test fabric with which the rubbing is carried out.
The results are illustrated in figure 12 and in the tables 12 and 13

Fig. 12 Samples of printed fabrics after the rubbing fastness verification





Tab. 12 Comparison of results depending on colour degradation

	Resistance to rubbing: DEGRADATION					
	Polyester		Cotton		Wool	
	Dry	Wet	Dry	Wet	Dry	Wet
Lutexal	4\5	5	5	4\5	5	4\5
Chitosan +Alginate	5	5	5	5	5	5
Chitosan	5	4\5	5	5	5	5
Alginate	4\5	4\5	5	5	5	5

An initial analysis of the results shows that the prints have generally maintained their colour, even though they have suffered greater degradation in the case of wet rubbing. As far as the behaviour of the fabrics is concerned, those of organic composition have shown the same properties both with dry and wet rubbing and have allowed to obtain the best results.
Regarding the compounds used, the most performing is the case of paste with alginate applied on fabric pre-treated with chitosan, immediately followed by the compound based on chitosan and by the one made with alginate.
the Lutexal compound, on the other hand, reveals the highest level of degradation of the print after testing, recording slightly lower values than its natural counterparts.

Tab. 13 Comparison of results depending on colour descharge

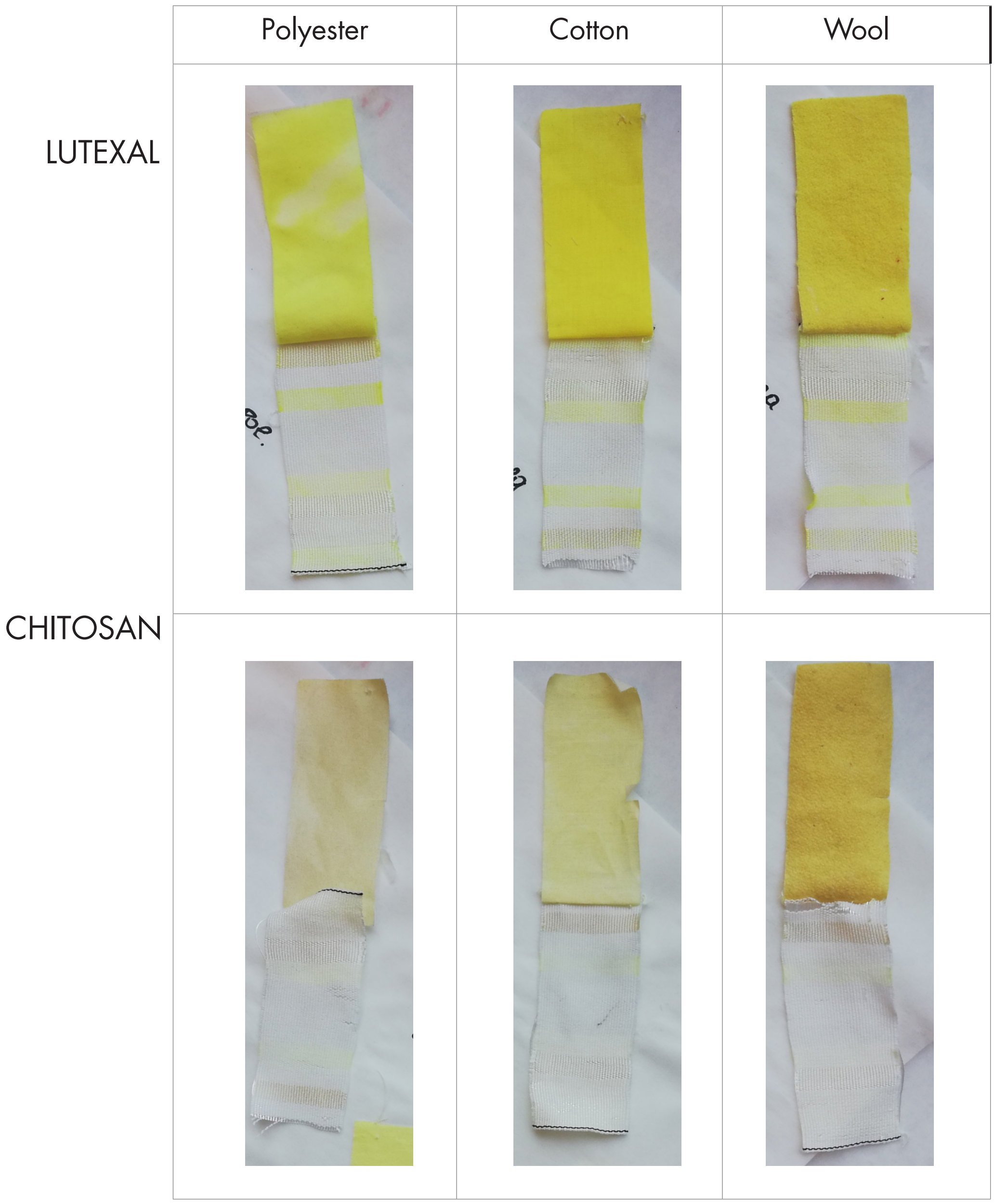
	Resistance to rubbing: DESCHARGE					
	Polyester		Cotton		Wool	
	Dry	Wet	Dry	Wet	Dry	Wet
Lutexal	4\5	4\5	4\5	4	3\4	2
Chitosan +Alginate	5	4	4\5	3\4	5	4
Chitosan	5	4	5	4	5	4\5
Alginate	5	1\2	5	4	5	4\5

With regard to the measurement of the colour discharge on the test fabric, it can be affirmed that the values are generally lower than in the previous case, especially when wet rubbing is involved.
In particular, the test shows that polyester has obtained higher results than its natural counterparts. This may be due in part to the reflectivity of the fabric surface, which makes it more difficult to identify the colour variation, and in part to the synthetic nature, which does not allow the tint to be easily affixed.
As far as the behaviour of the compounds is concerned, in this case the chitosan-based paste is the one with the best performance, followed by the other two natural prints and finally by the synthetic one, which is also the one with the worst values as regards the colour discharge.
The case of alginate-based printing is particularly interesting. This, in fact, always maintains a very high performance, except for the case of fastness to wet crooking when made on polyester, where the lowest data of all is recorded.

5.3.2 Washing fastness

This test assesses the performance of the printed fabric in terms of colour degradation and discharge after washing.
This consists of taking a sample of the printed material, which is then sewn with another adjacent textile, represented in fig. 13; The sample and the adjacent fabric are then washed together.
The detergent solution must be prepared at the temperature required by the method used and, after the soapy treatment, the sample is removed and rinsed in cold running water under a tap.
After the test fabrics have been wringed and dried, the colour change and staining shall be evaluated using grey scales.
The results are shown in figure 14 and in tables 14 and 15.

Fig. 14 Samples of printed fabrics after the washing fastness verification



	Polyester	Cotton	Wool
ALGINATE			
CHITOSAN + ALGINATE			

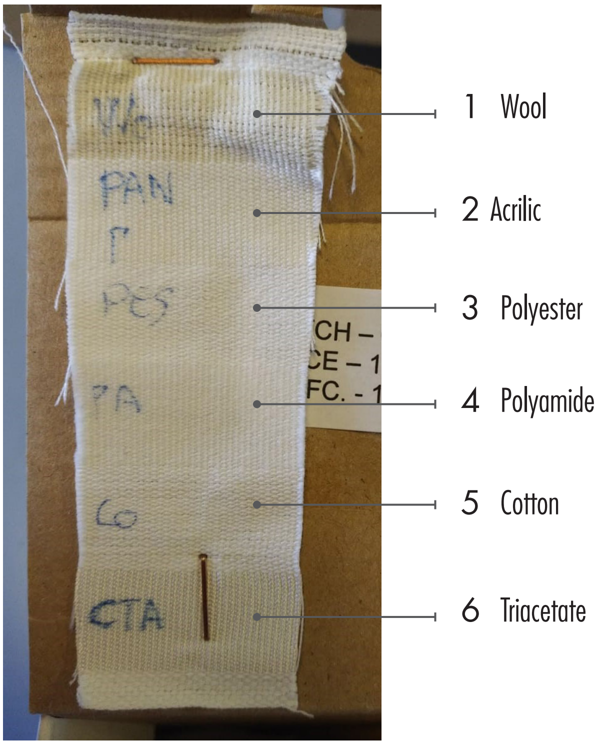
Tab. 14 Comparison of results depending on colour degradation

	Washing resistance: DEGRADATION		
	Polyester	Cotton	Wool
Lutexal	3\4	4\5	4
Chitosan+Alginate	2\3	4	4
Chitosan	4	3\4	4\5
Alginate	2\3	3	3\4

Based on the results of the test, it appears that the fabric with the highest level of degradation in most cases was polyester, especially when it comes to the application of alginate paste, both used alone and on fabric pretreated with chitosan.
Cotton and wool have very similar results, the former a little less than the latter. This can be explained by the thickness of the two fabrics: in fact the cotton has a lighter hand and soaks with soap more easily than the wool, which being more

consistent also proves to be more resistant to the action of the detergent.
As for the compounds, the most performing is the synthetic one, followed by the natural chitosan-based one.
The alginate paste applied to fabric pre-treated with chitosan gives excellent values on organic wool and cotton fabrics, but a lower performance in the case of synthetic polyester.

Sample intended to receive the colour discharged from the printed fabrics during washing.



Tab. 15 Comparison of results depending on colour descharge

	Washing resistance: DISCHARGE											
	Lutexal			Chitosan+Alginate			Chitosan			Alginate		
	Polyester	Cotton	Wool	Polyester	Cotton	Wool	Polyester	Cotton	Wool	Polyester	Cotton	Wool
1	3\4	4	4	4	4\5	4\5	4\5	4\5	4\5	3\4	4\5	4\5
2	5	5	5	5	5	5	5	5	5	5	5	5
3	4	4\5	4\5	4	4\5	4\5	4\5	5	4\5	4	4\5	4\5
4	3\4	3	3\4	3	4	4\5	4\5	4\5	4\5	3	4\5	4
5	4\5	5	4\5	4\5	4\5	5	5	5	5	4\5	5	5
6	5	5	5	5	5	5	5	5	5	5	5	5

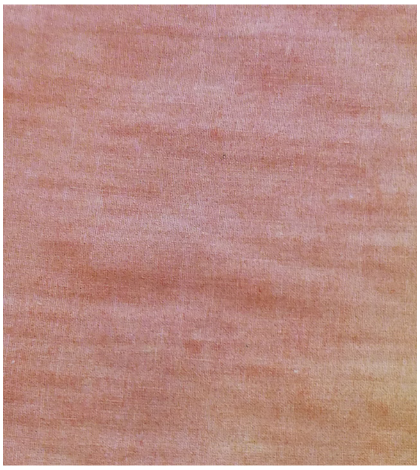
From a first analysis of the results, if we take into account the printing compounds used, we can see that the one that on average has shown the greatest fastness to washing is the chitosan-based paste, especially in the case of its application on cotton fabric.

The mixture that on the other hand has a higher average colour discharge is the one in which Lutexal is present, in particular when printed on polyester.
Focusing on the performance of the fabrics, it can be said that the natural ones generally presented a lower dispersion of hue, mainly in the case of wool. Fabrics with polyester composition, on the other hand, have generally been shown to resist washing less effectively.
As far as the sample on which the colour has been discharged is concerned, it can be deduced that the best values are obtained in the triacetate and in the acrilic compositions, even if excellent data have been obtained also with the cotton.
On the contrary, the polyamide textile brought to the greatest colour discharge.

Observations about the analysis of the fastness of the print:
Depending on the results obtained, it can be noted that as far as the resistance to rubbing is involved (Tab. 12 e 13), generally the fabrics on which chitosan has been applied, both as a pre-treatment and as a printing paste, are those that have shown the best values.
Considering the performance of the fabrics, respect to the level of degradation of the fabric test the most satisfactory parameters were recorded in cases of dry rubbing of cotton and wool, against those of dry rubbing of cotton and polyester in the case of the verification of color dispersion.
According to the washing resistance test, the formula containing chitosan has proved to be the most valid one as regards colour maintenance, especially in the case of its application on cotton (Tab. 15).
The compound containing lutexal, on the other hand, proved to be the least resistant in this area, as was the case linked to the level of sample degradation (Fig. 14).
The excellent performance of samples containing chitosan, used in the printing pulp or as a pre-treatment, is justified by the chemical bond that this compound creates with the fabric on which it is applied, binding the color more to the surface on which it is printed.
As far as the fabrics are considered, wool and cotton are those that in the tests have proved to be the most resistant to degradation and color discharge, to the detriment of polyester.
This phenomenon can probably be explained by the composition of the materials. In fact, wool and cotton, being of an organic nature, prove to be better surfaces with regard to the production of prints, when it is necessary to assess the fastness of the color to degradation and discharge. This is particularly relevant in the case of natural printing formulas, but also in the case of synthetic ones.
On the contrary, polyester, of artificial nature, proves in these cases to be a less favorable material for the realization of imprints, because it presents more difficulties in creating strong bonds with the paste that is applied to it.

5.4 Pretreatment with chitosan

Alginate printing paste on cotton

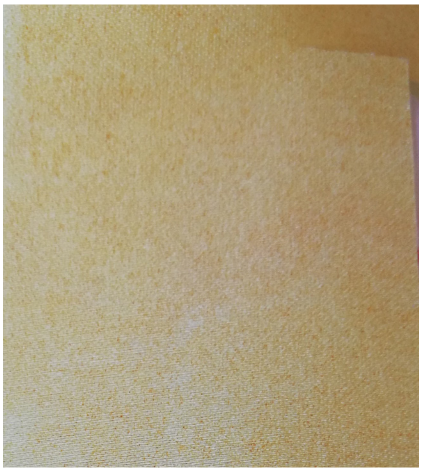


Cotton not pretreated with chitosan

Cotton pretreated with chitosan

Alginate printing paste on polyester

Polyester not pretreated with chitosan



Polyester pretreated with chitosan

Alginate printing paste on wool

Wool not pretreated with chitosan

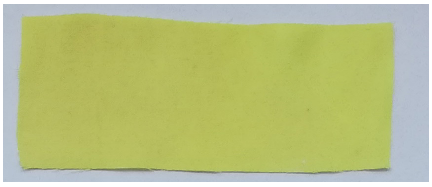
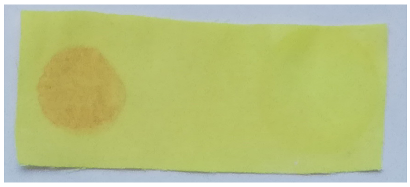
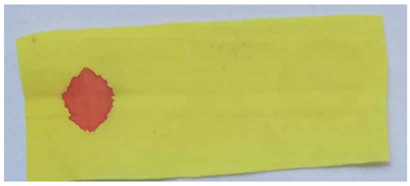
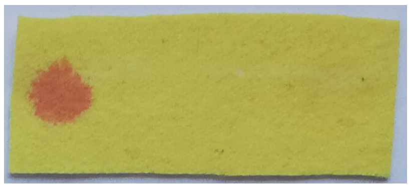
Wool pretreated with chitosan

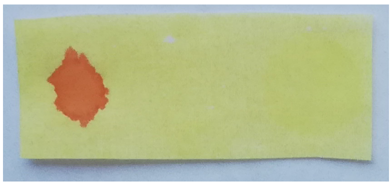
The result shows that the samples pretreated with chitosan have a bright yellow shade and, compared to the untreated fabrics, the former have a more uniform color.
Moreover, in the samples that have not been treated with chitosan, the shade is orange / yellow.
The most obvious case is that of cotton, where the print is almost orange.
Since the same formula had been applied to all the fabrics, the cause of the colour difference between the prints analysed was attributed to the action of chitosan.
For this reason, it was considered necessary to carry out a further PH verification test in order to examine the behaviour of the turmeric.

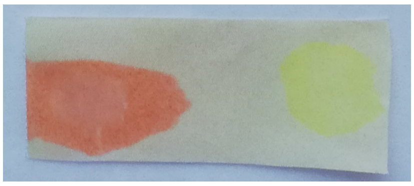
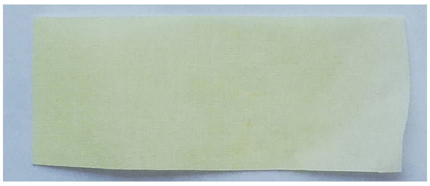
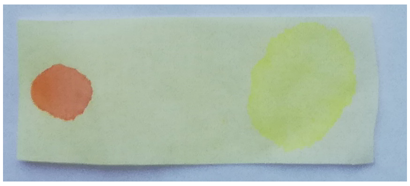
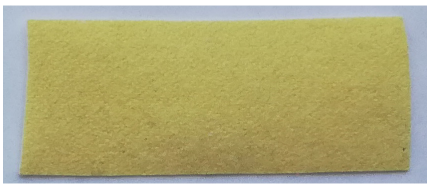
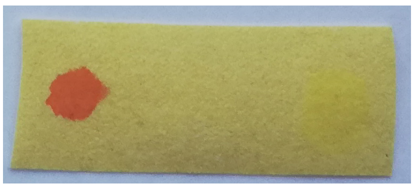
5.5 Halocromatic test

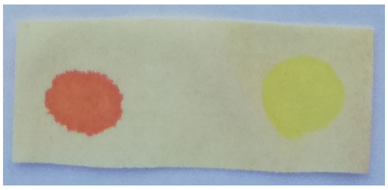
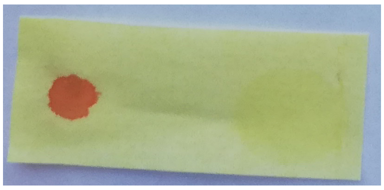
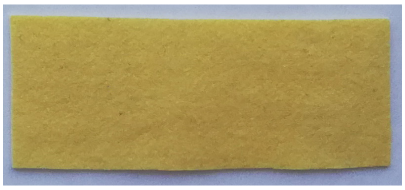
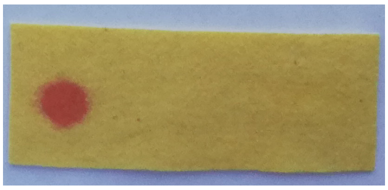
The result of applying the alkaline and acid solutions on the samples, respectively ofa pH correspondig to 9 and 4, on the left and right margins, is shown in the following figures.

Fig 6. Samples of printed fabrics before and after the PH verification

	LUTEXAL	
	Before the PH verification	After the PH verification
Polyester		
Cotton		
Wool		

	ALGINATE	
	Before the PH verification	After the PH verification
Polyester		
Cotton		
Wool		

	CHITOSAN	
	Before the PH verification	After the PH verification
Polyester		
Cotton		
Wool		

	CHITOSAN+ALGINATE	
	Before the PH verification	After the PH verification
Polyester		
Cotton		
Wool		

Observations about the evaluation of PH

At the first application of the acid and alkaline solutions, a reaction of the print colour was immediately verified.

In particular, it was possible to observe how, in a basic environment, the colour takes on a strong orange colour, visible on all the samples.

At the same time, in an acid environment it is possible to record an increase in the yellow shade, which is slightly less visible as the samples already have a rather accentuated shade of this type.

This analysis not only allows to verify the behavior of turmeric according to the level of acidity or alkalinity of the environment in which it is located, but also leads to further verify the strength of the color printed on the fabrics.

In fact in some cases, such as the application of Lutexal paste on cotton or wool, or the use on chitosan and chitosan wool followed by alginate, the area affected by the application of the acid solution has not visibly changed color, which enables to confirm that the print already has an intense yellow tone.

In other circumstances, however, as with all treatments carried out on polyester, or as regards the use of chitosan mixture on cotton, the acid solution has created an alteration in the colour of the print, making the tone of the yellow more saturated.

This leads to the assertion that the only application of the printing compound that has taken place before, in these circumstances has not been as effective as in the others as regards the final strength of the hue.
The current analysis is especially interesting with regard to the polyester compound fabric, which being synthetic makes it more difficult for the color to grip when making a print, especially when the compound has a natural origin.
The creation of an acidic environment in which the turmeric-based formula can act can therefore allow the creation of prints that offer a better strength of color even if applied on a less organic-friendly fabric such as polyester.

6.0 Conclusions

An experimental study was carried out to investigate processes, materials and formulas aimed at the production of natural prints on fabrics of different compositions, with the purpose to identify the best eco-sustainable methods for the realisation of prints on cotton, wool and polyester, comparing them with traditional synthetic processes in terms of strength and color fastness, resistance to dry and wet washing and rubbing.

After a study about the state of the art of natural printing processes, the most suitable formulas for the production of prints on fabrics have been identified, in relation to the pigments of rubia tinctoria and curcuma.

The previous research led to a further passage, which involved the realisation of both the natural prints, comprehensive of chitosan and alginate and the syntetic one, containing Lutexal, on cotton, wool and polyester.

An ulterior step brought to the making of imprintings with the alginate-based compound, applied on on the mentioned fabrics both pretreated with a chitosan solution and not, in order to compare them among themselves and with the results of the other formulas.
The resulting colour was defined as a pink tint with regard to the use of rubia tinctoria, due to the low concentration of pigment used in the production of the coating.
As far as the application of turmeric is concerned, the hue obtained was defined as bright yellow in almost all cases, with the exception of the prints made with natural compounds on polyester and the coating of chitosan paste on cotton, which, on the contrary, gave a more faded colour as a result.

Subsequently, the behaviour of the turmeric pigment according to the PH was studied, with the aim of further increasing the level of knowledge about the chemical behaviour of this pigment and the awareness of its use as a dye within a print.

It has been verified that under acidic PH conditions the pigment takes on a more intense yellow colour, while under alkaline PH it assumes a strong orange hue.

Finally, samples of each fabric and compound were analysed by measuring the strength and solidity of the colour and the resistance of the print in relation to wet and dry rubbing and washing.
As far as the values obtained thanks to the tests related to the strength of the colour are concerned, the compound based on Lutexal is the most intense one compared to all the others.
However, it should be mentioned that in the subsequent analyses of the fastness of the print, this compound was one of those with the lowest results, demonstrating the least resistance to washing and rubbing.
Regarding this point, it has to be taken into consideration that in the application of this paste no fixing product has been use, in order to imitate the performance of the natural mixtures.
In this case, on the contrary, the natural mixtures showed a better performance and in particular the case of the alginate paste applied on fabrics pretreated with chitosan.

In conclusion, once the results have been examined, it can be stated that natural printing mixtures based on alginate and chitosan can represent a valid alternative to synthetic mixtures in applications on fabrics of natural composition, given their resistance to washing and rubbing.
As for the strength of the colour, in order to obtain a tone equally intense to the synthetic counterpart, it will be necessary in their use to add a higher concentration of pigment to the mixture or, in the case of turmeric, to create an acidic environment so as to exploit the behaviour of the pigment to one's advantage.

Moreover, considering all the advantages that natural compounds offer for the protection of the environment and the health of consumers, these are a further reason to encourage and increase the research and use of these pastes.

6.1 Future lines

As far as the development of future lines is concerned, in view of the results, it has been concluded that it is necessary to improve organic printing pastes with the use of a natural product in order to improve the solidity of the former.
It is also considered necessary to analyse the process of alocromism through the employment of a standardised protocol.

7.0 Sources

1 Shahid, M., & Mohammad, F.; (2013). Perspectives for natural product based agents derived from industrial plants in textile applications-a review. Journal of cleaner production, 57, 2-18.
2 Gulrajani, M. L.; 2001. Present status of natural dyes
3 Sinha, K., Saha, P. D., & Datta, S.; 2012. Extraction of natural dye from petals of Flame of forest (Butea monosperma) flower: Process optimization using surface response methodology (RSM). Dyes and Pigments, 94(2), 212-216.).
4 Bhuyan, R., & Saikia, C. N.; 2005. Isolation of colour components from native dye-bearing plants in northeastern India. Bioresource technology, 96(3), 363-372
5 Cordis.europa.eu, Sustainable production of plant-derived Indigo, 2000- 2004
6 Bechtold, T., Mussak, R., Mahmud-Ali, A., Ganglberger, E., & Geissler, S.; 2006). Extraction of natural dyes for textile dyeing from coloured plant wastes released from the food and beverage industry. Journal of the Science of Food and Agriculture, 86(2), 233-242
7 Shams-Nateri, A; 2011 Reusing wastewater of madder natural dye for wool dyeing. Journal of Cleaner Production, 19(6-7), 775-781
8 Meksi, N., Haddar, W., Hammami, S., & Mhenni, M. F.; 2012. Olive mill wastewater: A potential source of natural dyes for textile dyeing. Industrial Crops and Products, 40, 103-10
9 Cardon, D. (2007). Natural dyes. Sources, tradition, technology and science, 268.
10 Blackburn, R. S. (2017). Natural dyes in madder (Rubia spp.) and their extraction and analysis in historical textiles. Coloration Technology, 133(6), 449-462
11 Robiquet, P-J, & Colin, J-J, 1826. Royal Botanic Gardens Kew, Medicinal Plant Name Service, mpns.kew.org; last accessed, 18 April 2017
12 J-J Colin and P-J Robiquet, Ann. Chim. Phys., 34 (1827)
13 Rochleder Justus Liebigs Ann. Chem., 80 (1851)
14 G C H Derksen, Red, Redder, Madder - Analysis and Isolation of Anthraquinones from Madder Roots (Rubia tinctorum), Dissertation, (Wangeningen University, 2001)
15 L Ford, C M Rayner and R S Blackburn, Phytochemistry, 117 (2015)
16 G Cuoco, C Mathe, P Archier, F Chematand C Vieillescazes, Ultrason. Sonochem., 16 (2009)
17 L Ford, R L Henderson, C M Raynerand R S Blackburn, J. Chromatogr. A, 1487(2017)
18 Y S Han, R V der Heijden, R Verpoorte, Plant Cell Tiss. Org., 67 (2001)
19 Boldizsár, Z Sz cs, Z Füzfai and I Molnár Perl, J. Chromatogr. A, 1133 (2006)
20 C Mouri and R Laursen, Microchim. Acta, 179 (2012)
21 J Wouters, Studies Conserv., 30 (1985)
22 R Hill and D Richter, Proc. Biol. Sci., 121 (1937)
23 G C H Derksen, H A G Niederlanderand T van Beek, J. Chromatogr. A, 978(2002)
24 Y Kawasaki, Y Goda and K Yoshihira, Chem. Pharm. Bull., 40 (1992)
25 E Y Backheet, S F Farag and N A El Emary, Bull. Faculty Pharm., 39 (2001)
26 E Schunck and L Marchlewski, J. Chem. Soc., 63 (1893)

27 A Vaidyanathan, Dyes Pigm., 6 (1985)
28 A M Tessier, P Delaveau and B Champion, Planta Med., 41 (1981)
29 Y Yasui and N Takeda, Mutat. Res., 121 (1983)
30 Vetter, A., I. Schwabe and A. Biertumpfel (1999) 'Ergebnisse zum Anbau und zur Ersverarbeitung von Farberpflanzen', in Gulzower Fachgesprache: Farberpflanzen 1999. Gulzow: Fachagentur Nachwachsende Rohstoffe, pp. 68-82
31 Marquard, R. and Siebenborn (1999) 'Zuchtung und Anbau von Krapp in Deutschland und der Turkey' in Gulzower Fachgesprache: Farberpflanzen 1999. Gulzow: Fachagentur Nachwachsende Rohstoffe, pp. 83-93
32 Jansen, P.C.M., "Curcuma longa L." In Jansen and Cardon, 2005. Pp.69-70
33 Green, C.L. 1995, "Natural colorants and dyestuff: A Review of production, markets and developement potential", FAO, Non wood forest products 4. Rome: food and agricolture Organzation of the United Nations
34 Li, S., Yuan, W., Deng, G., Wang, P., Yang, P., & Aggarwal, B. (2011). Chemical composition and product quality control of turmeric (Curcuma longa L.).
35 Acharya, N., & Roy, J. (2015). Is Turmeric Consumption Good For Health? Organic Chemistry, 1, 12.
36 Francis, F.J., 1999. "Colorants". St Paul, MN: Eagan Press
37 R. Schneider, S. Sostar-Turk: Good quality printing with reactive dyes using guar gum and biodegradable additives Dyes Pigm., 57 (2003), pp. 7-14
38 Fijan, R., Basile, M., Lapasin, R., & Šostar-Turk, S. (2009). Rheological properties of printing pastes and their influence on quality-determining parameters in screen printing of cotton with reactive dyes using recycled polysaccharide thickeners. Carbohydrate polymers, 78(1), 25-35.
39 Teli, M. D., Rohera, P., Sheikh, J., & Singhal, R., (2009). Use of Amaranthus (Rajgeera) starch vis-à-vis wheat starch in printing of vat dyes. Carbohydrate polymers, 76(3), 460-463.
40 Cloths, M. D., Rohera, P., Sheikh, J., & Singhal, R. (2009). Application of germinated maize starch in textile printing. Carbohydrate polymers, 75(4), 599-603.
41 Fijan, R., Basile, M., Šostar-Turk, S., Žagar, E., Žigon, M., & Lapasin, R. (2009). A study of rheological and molecular weight properties of recycled polysaccharides used as thickeners in textile printing. Carbohydrate Polymers, 76(1), 8-16.
42 M. A. M. (2004). Printing of Wool Fabrics with Anionic Dyes Using New Thickeners (Doctoral dissertation, Ph. D. thesis. Helwan University, Cairo, Egypt)
43 Ibrahim, N. A., Rashad, M. M., & Abo-Shosha, M. H. (2003). Polyacrylamide/Guar Gum Adduct as a New Thickener for Reactive Printing of Wool and Nylon-6. Polymer-Plastics Technology and Engineering, 42(5), 757-777
44 Abo-Shosha, M. H., Ibrahim, N. A., Allam, E., El-Zairy, M. R., & El-Zairy, E. M. (2006). Synthesis and characterization of polyacrylic acid/dexy 85 and polyacrylic acid/gum arabic adducts. Journal of applied polymer science, 101(6), 4290-4300.
45 Abo-Shosha, M. H., Ibrahim, N. A., Allam, E., & El-Zairy, E. (2008). Preparation and characterization of polyacrylic acid/karaya gum and polyacrylic acid/tamarind seed gum adducts and utilization in textile printing. Carbohydrate polymers, 74(2), 241-249

46 Prabhu, K. H., & Bhute, A. S. (2012). Plant based natural dyes and mordants: A. S. (2012). J. Nat. Prod. Plant Resour, 2(6), 649-664.
47 Padma, S., Vankar, R. S., & Avani, V., 2007). Enzymatic natural dyeing of cotton and silk fabrics without metal mordants. Journal of Cleaner Production, 15(1), 441-1.
48 Vankar, P. S., Shanker, R., Mahanta, D., & Tiwari, S. C. (2008). Ecofriendly sonicator dyeing of cotton with Rubia cordifolia Linn. using biomordant. Dyes and Pigments, 76(1), 207-212.
49 S.M. Burkinshaw, N. Kumar: The mordant dyeing of wool using tannic
50 H. Aminoddin. Functional dyeing of wool with natural dye extracted from berberis vulgaris wood and Rumex hymenosepolus root as biomordant. Iran. J. Chem. Chem. Eng., 29 (2010), pp. 55-60
51 H.F. Mansour, S. Heffernan. Environmental aspects on dyeing silk fabric with Sticta coronate lichen using ultrasonic energy and mild mordants. Clean Technol. Environ. Policy, 13 (2011), pp. 207-213
52 K.H. Prabhu, M.D. Teli. Eco-dyeing using Tamarindus indica L. seed coat tannin as a natural mordant for textiles with antibacterial activity. J. Saudi Chem. Soc. (2011)
53 K.H. Prabhu, M.D. Teli, N.G. Waghmare Eco-friendly dyeing using natural mordant extracted from Emblica officinalis G. Fruit on cotton and silk fabrics with antibacterial activity
Fiber. Polym., 12 (2011), pp. 753-759
54 A.K. Samanta, A. Konar, S. Chakraborti, S. Datta Dyeing of jute fabric with tesu extract: Part 1 – effects of different mordants and dyeing process variables Indian J. Fibre Text. Res., 36 (2011), pp. 63-73
55 S.V. Singh, M.C. Purohit. Applications of eco-friendly natural dye on wool fibers using combination of natural and chemical mordants. Univers. J. Environ. Res. Technol., 2 (2) (2012), pp. 48-55
56 Guesmi, A., Ladhari, N., Hamadi, N. B., Msaddek, M., & Sakli, F. (2013). First application of chlorophyll-a as biomordant: sonicator dyeing of wool with betanin dye. Journal of cleaner production, 39, 97-104.
57 Prabhu, K. H., & Teli, M. D. (2014). Eco-dyeing using Tamarindus indica L. seed coat tannin as a natural mordant for textiles with antibacterial activity. Journal of Saudi Chemical Society, 18(6), 864-872
58 K. CammannBiosensors based on ion-selective electrodes Fresen Z Anal Chem, 287 (1977), pp. 1-9
59 Mehrotra, P. (2016). Biosensors and their applications: a review. Journal of Oral Biology and Craniofacial Research, 6(2), 153-159.
60 Thévenot, D. R., Toth, K., Durst, R. A., & Wilson, G. S. (2001). Electrochemical biosensors: recommended definitions and classification. Analytical letters, 34(5), 635-659.
61 Mehrotra, P. (2016). Biosensors and their applications–A review. Journal of oral biology and craniofacial research, 6(2), 153-159.
62 Hao, S., Wu, J., Huang, Y., & Lin, J. (2006). Natural dyes as photosensitizers for dye-sensitized solar cell. Solar energy, 80(2), 209-214.
63 Wongcharee, K., Meeyoo, V., & Chavadej, S. (2007). Dye-sensitized solar cell using

natural dyes extracted from rosella and blue pea flowers. Solar Energy Materials and Solar Cells, 91(7), 566-571.

64 Attanayake, C. I. F., De Silva, C., Premachandra, B. A. J. K., De Alwis, A. A. P., & Senadheera, G. K. R. (2019). Dye-sensitized solar cells: using over 100 natural dyes as sensitizers

65 L.Van de Schueren and K. De Clerk, Color technol., 128, 82, 2012

66 Devarayan, K., & Kim, B. S. (2015). Reversible and universal pH sensing cellulose nanofibers for health monitor. Sensors and Actuators B: Chemical, 209, 281-286.

67 Giachet, F. T., Vineis, C., Ramirez, D. O. S., Carletto, R. A., Varesano, A., & Mazzuchetti, G. (2017). Reversible and washing resistant textile-based optical pH sensors by dyeing fabrics with curcuma. Fibers and Polymers, 18(4), 720-730.

68 Mirjalili, M., & Karimi, L. (2013). Antibacterial dyeing of polyamide using turmeric as a natural dye. Autex Research Journal, 13(2), 51-56.

69 Suwantong, O., Opanasopit, P., Ruktanonchai, U., & Supaphol, P. (2007). Electrospun cellulose acetate fiber mats containing curcumin and release characteristic of the herbal substance. Polymer, 48(26), 7546-7557.