DEVELOPING ECO-FRIENDLY UV PROTECTIVE TEXTILES BASED ON PLANT EXTRACT.

Kirti Ghosh[1], Asimananda Khandual[2], Bijayalaxmi Sahoo[3]
Department of Textile Engineering, CET, Bhubaneswar

Abstract:- Frequent exposure to solar ultraviolet (UV) radiations due to the depletion of the ozone layer is the major risk factor for causing premature ageing of the skin, damage to eyes, sunburn, sunstroke deaths and cancers since last decades. In recent years, there has been much concern about growing levels of UV radiation in the sunlight, mostly during the summer months. Sunscreen formulations have been optimized to become protective over a broader spectrum of UV radiation using organic as well as inorganic components to maintain greater photo-stability. Further, developing textiles with UV protection functionality has been widely researched up to now. The government has taken major initiatives; mostly related to awareness, prevention of working hours in peak times etc. There exist a few complex processes for high-end application at prohibited cost. At the outset, a low cost and effective process of making UV protective textiles is the need of the hour that could potentially be much beneficial to the society. The comprehensive focus of this article is to develop effective, eco-friendly and low-cost UV-protected textile fabric for practical use based on plant extract.

***Keywords:*-UV protection factor (UPF), Sun protection factor (SPF), UV absorbers, Cotton fabric, Sunscreen, Anti-oxidants.**

1. Introduction:

Ultraviolet radiation is a part of the electromagnetic spectrum (as shown in figure-1) that reaches the earth from the sun with wavelengths shorter than visible light making it invisible to the naked eye. Since, skin is the largest organ of the human body, the importance of maintaining homeostasis and protecting the skin from ultraviolet radiation (UVR) is important, otherwise, it can result into wrinkles, hair loss, blisters, rashes, life-threatening cancers, and disorders in immune regulation. Primarily prevention of skin cancer includes -using sunscreens or wearing protective clothing in order to reduce the risk of skin cancer but for many reasons, these primary prevention approaches have met with limited success.

UV rays are classified into three types—A, B and C. UV-C percolates due to ozone layer while A and B reaches Earth. UV-A is advantageous for health but B becomes dangerous when it crosses the limit. It causes sunburns and can be the cause of skin cancer and cataract. The main reason for high UV index may be that the sun is almost vertical in the month of May. If temperature increases, UV rays will also increase causing aggravated risks from the heat waves. The penetration of different wavelength of UV rays into our skin is shown in figure-2.

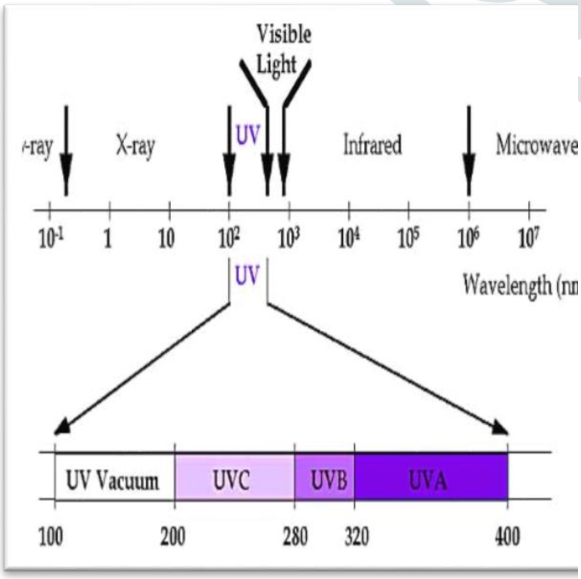

Figure 1 - Electromagnetic spectrum.
Source: http://www.bioscience.org/1997/v2/d/soehnge

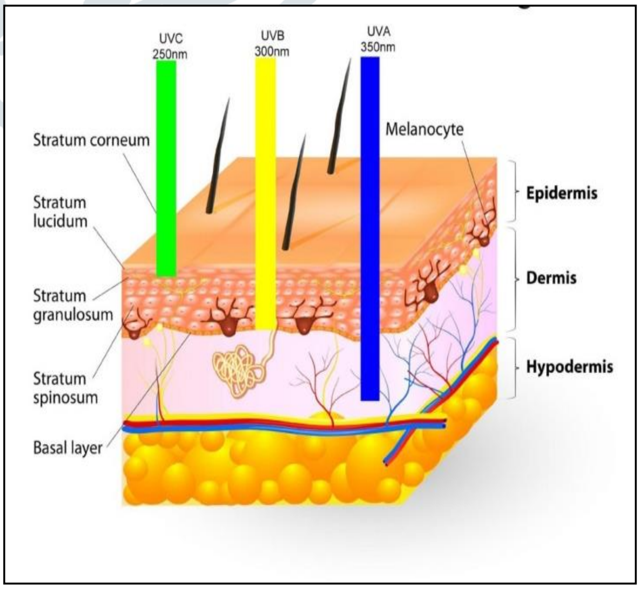

Figure 2-Penetration of different UVwavelengths into skin
Source: https://www.adamscheinermd.com/h

2. UV radiation:

Unraveling the mysteries associated with ultraviolet rays, their properties, and their effects on numerous living creatures have been a gradual method spanning to the length of just about three centuries ranging from the seventeenth century [1 – 6]. Terms like near UV ((290 – 400 nm), far UV (180 – 290 nm) and vacuum UV (below 180 nm) have been coined by physicists based on the properties of these actinic radiations. UVA is found in the region of 320 – 400 nm, UVB represents the region between UV C and UVA, i.e. 290 – 320 nm, and UVC region represents the region below 290 nm. The order of efficiency has been set as UVC > UVB > UVA >. The proportion of the actinic radiation region is about 5 – 6 % of the total incident radiation, and therefore the quantum energy of UVR is comparable to the bond energies of organic molecules [1 - 3, 7 – 10].

3. UV exposure and human skin:

Basically, solar ultraviolet radiations have an effect on numerous factors that include sun's altitude, geographical position, altitude, the ozonosphere, scattering within the atmosphere, environmental and other related conditions. Abundant analysis has been carried out to assess the impact of the Ultraviolet illumination rays on numerous living organisms, particularly humans [10, 11 – 18] and the relationship between carcinoma and UV dosage is well correlated. Skin cells that receive daylight absorb harmful UV radiation and slough off to eliminate harmful Ultraviolet illumination from the body. However, the absorption of an excessive amount of UVR results in scars which will induce diseases like basal cell carcinoma and squamous cell carcinoma(together referred as non melanoma skin cancer) ,melanoma and erythema as shown in figure-3 Excessive UV radiation leads to cell harm and causes inflammation of the human skin, the apparent consequences of which is erythema or sunburn [12]. The total UVR dose reaching the skin is an important factor in the occurrence of both erythema and carcinoma, although there is no evidenced link between erythema and carcinoma [15].

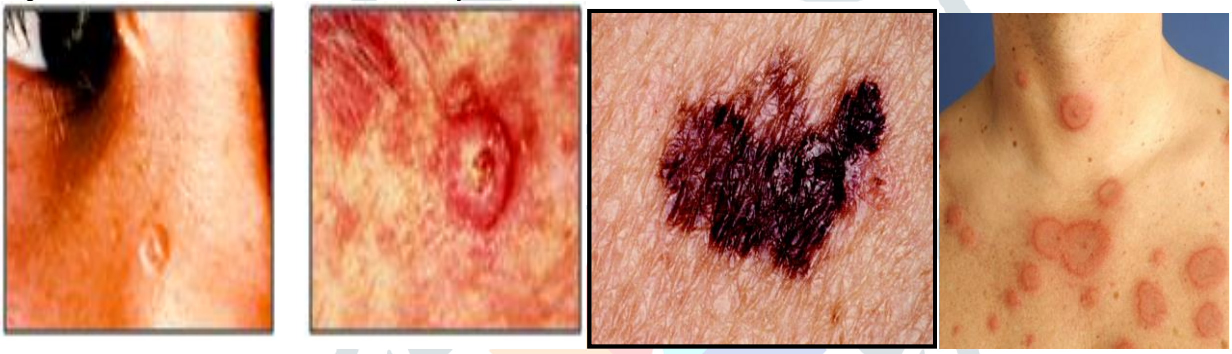

Figure 3- Basal cell and Squamous cell carcinoma Melanoma Erythema

There are six basic types of skin categorized according to the tendency of pigmentation which demand different levels of ultraviolet illumination protection [9, 10, 16, 19 – 22] as shown in Table 1and Figure 4.

Table 1. Effect of UV rays on different types of skin

	Critical dose mJ/cm^2	Self-Protection time (min)	Risk level
I – White	15 – 30	5 - 10	Burns easily has the highest risk of premature skin ageing and the greatest risk of developing skin cancer
II – White	25 – 35	8 – 12	Burn and only rarely tan
III – Brownish	30 – 50	10 – 15	Tan and occasionally burn
IV – Brown	45 – 60	15 – 20	Tan and occasionally burn
V – Brown	60 – 100	20 - 35	Adequate levels of melanin and rarely burns, easily tan
VI – Dark Brown – Black	100 – 200	35 - 70	Adequate levels of melanin pigment provide protection. Very rarely burns, easily tan

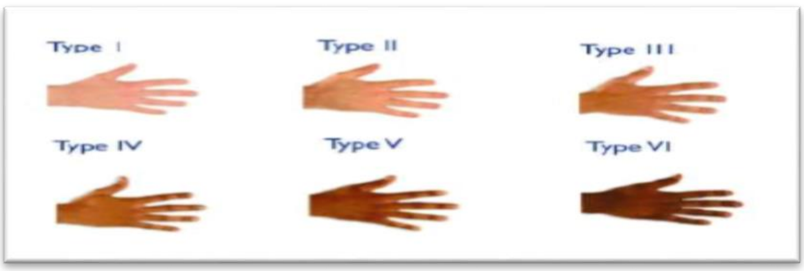

Figure 4- UV exposures to Human Skin types.

The minimal erythemal dose (MED) is apparently consistent with a fair complexion but shows variations among people of types III and IV. For practical purposes, the population could be broadly distinguished into two main groups, i.e. sensitive and less sensitive individuals [22].

4. Ultra-violet protection factor:

UPF and SPF are different terminologies related to the protection given by the textile materials, accessories and sunscreen lotions[7, 12, 14, 15, 21, 29]. Risk estimates of unprotected skin, protect skin and UPF are given by the following formulae:

$$\text{risk unprotected} = \sum S\lambda\ A\lambda$$

$$\text{risk protected} = \sum S\lambda\ A\lambda\ \Delta\lambda\ (\text{from } A\lambda \text{ to } T\lambda)$$

$$\text{UPF} = \text{risk unprotected} / \text{risk protected}$$

where $S\lambda$ is denoted as source spectrum ($Wm^{2}nm^{-1}$), the transmittance is denoted as $T\lambda$, $A\lambda$ is denoted as action spectrum for measured response and $\Delta\lambda$ is denoted as bandwidth in nm. Since the relative erythemal spectral effectiveness is higher within the UVB region compared to the UVA region, the UPF values rely totally on the transmission within the UV B region [3]. UV rays falling on textiles are partly reflected, absorbed and partly transmitted through the fibres & interstices, and the optical porosity of a fabric limits its potential to provide protection against UVR. The solar protection factor (SPF) is defined as a quotient from a harmful dose without sun protection and a harmful dose of sun protection. This can be estimated from erythemal effectiveness (EW (λ)), (P(λ)) and from the wavelength-dependent transmission of the sun protection agent [12]. The distinction between the values of UPS and SPF arises principally owing to the 'hole effect' within the materials.

5. Effect of UV radiation on textile materials:

UV radiation is one in each of the key causes of degradation of textile materials, that is a result of excitations in some elements of the polymer molecule and a gradual loss of integrity and depends on the nature of the fibres [8, 30 – 38]. Textile materials are susceptible to get influenced by light and other environmental factors due to very large surface-volume ratio. In nylon, the penetration of UV radiation causes photo-oxidation and leads to decrease in elasticity, tensile strength and a small increase in the degree of crystallinity [33, 35]. The loss in tensile strength with the absence of ultraviolet filters appears to be higher in the case of nylon (100% loss), followed by wool, cotton and polyester, with approximately 23%, 34% and 44% respectively after exposure of thirty days[36]. Elevated temperature and UVB radiation on cotton plants end in severe loss of bolls [38]. Coloured forms of cotton that occurs naturally contain pigment ranging from light green to tan brown and inherent long-run ultraviolet protection properties [61] with a UPF of 64 and 47, whereas normal cotton shows a UPF of 8.

6. UV absorbers:

UV absorbers are defined as the organic or inorganic colourless compounds with strong absorption in the UV range of 290 – 360 nm [8, 12, 13, 20, 30, 36, 39 – 46]. When the fibres are incorporated with UV absorbers, electronic excitation energy is converted into thermal energy and thus, acts as radical scavengers. The high-energy, short-wave ultraviolet radiation excites the UV absorber to a higher energy state and then the energy absorbed is dissipated as longer-wave radiation [13,48,47]. Most widely used absorber i.e. 2-ethyl hexyl-4-methoxy cinnamate makes a considerable contribution to the 'refractive index matching' of skin[48]. An effective UV absorber must be able to absorb throughout the spectrum to remain stable against UVR and to avoid degradation or loss of colour [36].

Organic UV absorbers are primarily derivatives of o-hydroxy benzophenones, o-hydroxy phenyl triazines, o-hydroxy phenylhydrazines [8, 13, 30]. The ortho-hydroxyl group is considered vital for the absorption and to make the compound soluble in alkaline solution [36]. UV absorbers that are commonly used include 2-hydroxyphenyl benzotriazoles, 2-hydroxy benzophenones, 2-hydroxy phenyl-S- triazines and chemical absorbers such as benzoic acid esters and hindered amines are also used[40].Organic products like benzotriazole, hydro benzophenone and phenyl triazine have low energy levels, low sublimation fastness and good diffusibility and are mostly used for coating and padding processes in order to achieve broad protection against ultraviolet rays [12]. Orthohydroxy phenyl and diphenyl triazine derivatives have an excellent sublimation fastness, and a self-dispersing formulation and is suitable for high-temperature dyeing in pad- baths and also in printing pastes [44].

To improve the light fastness and the weatherability of spun-dyed fibres UV absorbers are incorporated into the spinning dope prior to the fibre extrusion and dyeing bath[36, 49]. UV absorbers to the extent of 0.6 – 2.5% are sufficient to provide UVR protection fabrics [9]. UV absorbers present in PET, nylon, silk and wool protects the fibres against photodegradation caused due to sunlight. The photo-yellowing defect that occurs in wool fibre on exposure to sunlight can be minimized by using UV absorbers. [13]. Triazine class-hindered amine light stabilisers are used in PP to improve the UV stability. The addition of HALS to 0.15% weight is sufficient to improve stability substantially. Even pigmented PP requires UV stabilisers if the fibres are exposed to UV during their services [43]. High-energy UV absorbers suitable for PET include derivatives of o-hydroxyphenyl diphenyl triazine.These absorbers can be used in dyebaths or printing pastes.

UV absorbers with refractive index > 2.55 give maximum opacity and covering capacity [12].The inorganic pigments present in the fibre provides better protection due to the reflection of light from the substrate [9, 12, 30, 32, 50 – 52]. TiO_2 acts as UV absorber when added in the spinning dope and produces matt effect in the fibres [8]. The absorption capacity of Titanium dioxide and ceramic materials in the UV region lies between 280 and 400 nm and reflects the visible and infrared rays [53]. These two absorbers are also used as dope additives and to achieve maximum effect, these particles are often applied in one bath [9, 12, 30, 54].

Nanoscale titanium gel particles strongly bound to the cotton fabrics can give a UPF ≥ 50 without impairing the tensile properties. Brighter provide the highest UV transmittance compared to the dull pigmented viscose yarns, modal yarns [55]. Zinc oxide nanoparticles, which have a very narrow size distribution (20-40 nm) and minimal aggregation, can result in higher levels of UV blocking [51]. A mixture of (67/33) titanium dioxide and zinc oxide on cotton and nylon fabrics provide better absorption of UVR than that of used individually [32]. Microfine nylon fabrics with a porosity of 0.1% are capable of giving UPF > 50 with 1.5% TiO_2 [52]. If the UV absorbers are incorporated during dyeing then there is a decrease in the dye uptake slightly, except in post-treatment application [40].

Many commercial products and processes have been developed to produce fabrics with a high level of UPF using various dope additions and topical application methods[1, 7, 10 - 12, 20, 36, 44, 56, 57].Most of the commercial products are compatible with the dyes or can be used as finishing agents in the application to the textile materials, and these agents can be applied using simple padding, the exhaust method, the pad- thermo -fix and the pad-dry-cure methods [7, 36, 39, 56, 58].

7. Textile materials and UV protection:

Sun protection involves a mixture of sun avoidance along with the use of protective garments & accessories [15, 16]. Reducing the exposure time to daylight, using sunscreens and use of protective apparels are the three ways of protection against the harmful effects of ultraviolet radiation [17]. Apart from sunscreen lotions, textile materials and accessories are largely used for ultraviolet protection [2, 3, 7, 10, 12 – 14, 16, 25, 26, 33, 35 - 39, 45, 46, 51, 58, 60 – 67]. UV protection through textiles includes numerous apparels, accessories like hats, shoes, shade structures such as umbrellas, awnings, baby carrier covers, etc. UV consumer goods are intended specifically for fighting off a lot of UV rays with tighter weaves and special coatings that facilitate to absorb the rays. Clothes are labelled based on a rating system for apparel referred to as ultraviolet protection factor (UPF), a 15 to 50+ worth representing the extent of protection. As the SPF in sunscreen likewise, the higher the UPF, the higher the ultraviolet ray protection.

8. Dyeing & finishing:

The use of dye or pigment, the absorptive groups present in the dyestuff, depth of the shade after dying, uniformity of dye penetration and additives used in dyeing determines ultraviolet protection capabilities of the textile materials [3, 7, 16, 35, 39, 41, 60, 64, 67].Better transmission of UV radiation is observed in the case of bright fibres specifically viscose than in case of dull fibres [39]. Heavyweight fabrics are not comfortable for summer conditions. So, to achieve a protective effect, dyeing and printing is the most suitable method of application. Darker colours of the same fabric type (black, navy, dark red) absorb UVR much more strongly than the light pastel colours for identical weave with UPF, in the ranges of 18 – 37 and 19 –34 for cotton and polyester respectively [3, 35]. Some direct, reactive and vat dyes are capable of giving a UPF of 50+ [16]. Some of the direct dyes substantially increase the UPF of bleached cloth, which depends on the relative transmittance of the dyes in the UV B region. UPF calculated using a direct dye solution in most cases appears to be higher than that of the fabric after dying as the theoretical concentrations are often higher than the actual concentration.

Cellulosic fabrics transmit UVA and UVB equally with the transmittance ratio (T_A/T_B) 0.9. The UPF increases from 4.7 to 5.0 – 14.0 when dyed with the reactive dyes, depending upon the concentration, which is insufficient to satisfy the minimum requirements [60]. Some of the vinyl sulphone dyes and monochlorotriazine dyes possess UVR absorption characteristics, which also increase the concentration. When cellulosic fabrics are dyed with these sulphone dyes, they show a reduced UVR transmission from 24.6% to 10-20% and 27.8% to 8-22% for UVA and UV B respectively. When mixtures of these dyes are used, the UPF increases synergistically. Some combinations of dispersing reactive mix can give prolonged UV protection with a UPF of 50+ for P/C blends [46].

The effect of optical brightening agents on UPFs at the finishing operations, as well as in the wash cycles, has been demonstrated extensively in the past [7, 16, 42,46, 62, 67, 71, 72]. OBA enhances the whiteness of textiles by UV excitation and visible blue emission and this phenomenon of excitation and emission is caused by the transition of electrons involved in p-orbital either from conjugated or aromatic compounds [46].The excitation maxima of most optical brighteners lie within the range of 340 – 400 nm. The UPF of cotton and cotton blends can be improved by OBA, but it is not possible in case of the fabrics that are 100% polyester or nylon [16]. The presence of OBA in the P/C blends (67/33) to the extent of 0.5% can improve the UPF from 16.3 to 32.2, which is more or less close to that of the UV absorbers with 0.2% (UPF 35.5). After washing, there is a loss of UPF in the case of OBA-treated fabrics, and the UPF reaches the level of that in the untreated fabric after 10 washes. Another limitation of many OBAs is that they mostly absorb in the UVA part of the daylight spectrum (93%) but have a weak absorption in UV absorption around 308 nm (92%), which plays an important role in skin disease [6, 71].

9. UV protection care labeling:

Initiatives for developing standards related to ultraviolet protection started in the 1990s, and standards related to the preparation of fabrics, testing and guidance for UV protection labelling have been formulated [12, 76, 77, 78] by different agencies. Care labelling similar to fabric and garment care labels has been developed for UV protection, and standard procedures have been established for the calculation, measurement, labeling methods and comparison of label values [12, 26, 61, 64, 71, 76, 77, 79 - 82] for textile products. Since 1981, the Skin Cancer Foundation, an international body, has offered a seal of recommendation for the photoprotective products which include sunscreens, sunglasses, window films and laundry detergent additives, in accordance with AATCC TM 183 or AS/NZS 4399; the products recommended are reviewed annually [61].

Table 2. Grades and classification of UPF

UPF	Transmission (%)	Classification	Grade
> 40	< 2.5	Excellent protection	III
30-40	3.3 – 2.5	Very good protection	II
20-29	5.0 – 2.4	Good protection	I

Besides other labelling requirements of garments including permanent care labels and fibre content labels, UV labelling is an additional requirement. Apart from the UPF label, block numbers can also be used based on the ultraviolet transmittance value in their respective UVR range [26, 61]. Table 2 shows the different grades and the related protection factors for the textile materials. The UPF value to be placed on the label is that of the sample, reduced by its standard error of UPF values, and then rounded down to the nearest multiple of 5 but not greater than 50. For example, a fabric with a UPF rating of 20 only allows $1/20^{th}$ (5%) of the sun's UV radiation to pass through it and blocks about 95% of UV rays when worn [71].

10. Potential of plants in UV Protection:

Traditional use of herbs in medicines and cosmetics is prevailing for centuries. The potential of herbs to combat skin diseases is well-known for their antioxidant activity [88]. As, ultraviolet radiation causes sunburns, wrinkles, premature ageing and cancer; there is an increasing demand for protection from UV radiation and prevention from their side effects.

Plant-derived products have many antioxidant properties that are effective against harmful UV radiations. Important categories of beneficial phytoconstituents with antioxidant compounds mainly include flavonoids, phenolic acids and high molecular weight polyphenols. Researchers showed that green and black tea (polyphenols) improves adverse skin reactions and provides protection to UV exposure. Spectrophotometer testing shows that as a concentrated extract of Krameria triandra absorbs 25 to 30% of the amount of UV radiation typically absorbed by octyl methoxycinnamate present in it [89, 88].

A recent work carried out in developing UV protection finish on cotton fabric using Betel leaf [86] extract by exhaustion method which imparted excellent protection against UV rays showing UPF rating 56.UV protection properties were studied on cotton fabrics with the application of aqueous and methanolic extracts of two different plants, i.e., Achyranthes aspera and Alhagi maurorum [87]. Thus, using natural ingredients to prevent UVR is becoming very popular today due to its non-toxic properties and are available easily at a low cost.

11. Conclusion:

Since the stratospheric ozone layer is steadily decreasing due to growing consumption of conventional fuels; it has led to increased UV radiations. These harmful radiations have prompted an urgent alert throughout the globe, as the world has already seen the endangered ecological unbalance since last 2-3 decades. UV index of 0 to 4 is classified as no risk category while 4-5 has low risk. If the UV index reaches 5 to 7 range, it means it has medium health risk on health; and 7 to 10 carries high risk, above 10 is extremely dangerous [83]. So, it is essential to protect exposure of skin from an excessive amount of UV radiations. Reducing the exposure time to sunlight, using sunscreens and protective clothes are the three ways of protection against the harmful effects of UV radiation. In recent years, research on textile materials embedded with chemical UV absorbers and incorporation of TIO_2 nanoparticles has been paying a tremendous attention towards protection from UV-A and UV-B radiation. However, there are certain limitations in using chemical UV absorbers due to its toxicity, high cost and weak washing fastness. Recently some researchers are investigating in applying aqueous and methanolic extraction of different plants in terms of protection from UV radiation [85,87]. Phyto-constituents are gaining popularity as ingredients in cosmetic formulations and have many antioxidant properties that are effective against harmful UV radiations.

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