Q - switched laser removal of tattoos- A clinical and spectroscopic investigation of the mechanism

K. Siomos[1], R.T. Bailey[2], F.R. Cruickshank[2], M.J. Murphy[3]

[1]Institute of Materials Structure and Laser Physics, Technical University of Crete, 73110 Chania, Crete, Greece
[2]The Department of Pure & Applied Chemistry, The University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland
[3]Mysan Medical Ltd., Glasgow, Scotland

ABSTRACT

The liquid phase spectra of tattoo pigments are shown to be unreliable as a basis for mechanistic deductions. The reflectance spectra of the solids from 2000 nm to 500 nm (5000 to 20000 cm^{-1}) are shown to accurately assess the relative loss of laser light for different pigments and to be useful in examining these to check for similarities in the pigments. The absorbance differences between the pigments are shown to be largely irrelevant in assessing the ease of tattoo removal by laser radiation of a variety of wavelengths. A multiphoton absorption mechanism with its concomitant shock wave is proposed to be responsible for the reduction of pigment particles to small sizes which the lymph system can remove. The different behaviour of blue and green tattoos, treated by Q-switched ruby and Nd:YAG lasers, is attributed to the particle aggregation size of the pigments in the tattoo.

Keywords : Tattoo, Clinical treatment of tattoos, Tattoo-pigments' spectroscopy, Pigment characterization, Nd:YAG laser, Ruby laser, Alexandrite laser, Multiphoton absorption, Shock waves

2. INTRODUCTION

The properties of laser light in biological applications can be efficiently exploited only if the mechanisms of the relevant processes are well understood [1-6]. Such mechanisms are not simple, since laser light of high intensity is frequently used (in terms of Joules per square centimetre-fluence or Watts per square centimetre-flux). Photophysical and photochemical processes resulting from this type of radiation differ markedly from those of low intensity radiation as obtained from even the most powerful lamps. The successful approach to the treatment of skin disorders or artificially induced skin discolouration as in tattoo engraving depends strongly on the mechanism of the transfer of energy from the laser beam to the relevant tissue or pigment[7-9]. When light is incident upon a medium such as skin with an embedded pigment, it is reflected partially at each mismatch of refractive index,i.e., at each material boundary. In the case of tattoos, this would be at the air/skin interface and at the tissue/pigment interface. Additionally, the light is partially scattered by inhomogeneities in the refractive index which in our example would principally be the transparent boundaries in the tissue. Finally, the light is absorbed partially by both the tissue and the pigment. Only this last process leads to energy transfer into the pigment particle, ultimately causing physical and chemical transformations. However the first two of these processes lead to loss of energy from the laser beam arriving at the target site and lead indirectly to effects on the perceived success of the clinical procedure. It is accordingly necessary to consider their contribution as well as the absorption process.

0-8194-1987-7/96/$6.00

Absorption as observed in a spectrometer (low light intensity conditions - ca 10^{15} photons cm^{-2} s^{-1}) results from the transfer of energy from the laser beam to excited states of the pigment molecules or ions. These may be electronic, vibrational excited states. Eventually, all of these excited states will either emit the radiation at longer wavelengths (fluorescence or phosphorescence) or they will convert the energy to heat and warm the sample. Fluorescence and phosphorescence are significant only for electronically excited states for which these may lead to substantial loss of energy being non-directional. We shall show that these effects are negligible. In a spectrometer, the heating effect is trivial. This is not so for laser experiments, however [8,9]. In laser work the light intensity is very high (ca 10^{28} photons cm^{-2} s^{-1}). If we consider the lifetime[10] of the relevant vibronic excited state as 10^{-11} s, and a molecule as 100^2 A in area (10^{-12} cm^2), it is clear that at low light intensities a given molecule interacts with 10^{15} x 10^{-12} x10^{-11} = 10^{-8} photons during the excited state's dephasing lifetime or possibly 10^{15} x 10^{-12} x10^{-9} = 10^{-6} photons in the electronic excited state's total lifetime of, typically, 1 ns. In practice this means that a molecule can only interact with one photon at a time under these conditions. However, at the high laser intensities a molecule can interact with 10^{28} x10^{-12} x10^{-11} = 10^{5} photons in the vibronic lifetime or 10^{7} photons in the state's total lifetime. This process leads to multi - or multiple - photon absorption depending on whether the excited state has retained phase or not before the second photon interaction occurs. With reference to the present study, a Q-switched ruby laser, operating at 694 nm and a maximum energy density of 12 J cm^{-2} with a 25 ns pulse width, corresponds to $(hc/\lambda)^{-1}$x pulse energy / pulse duration = $(6.626 \times 10^{-34} \times 3 \times 10^{8} / 694 \times 10^{-9})^{-1}$ x12/(25×10^{-9}) = 1.67×10^{27} photons s^{-1}. If this laser pulse is applied to a 5 nm diameter spot, the laser flux becomes, $1.67 \times 10^{27} / (3.142 \times 0.25^2) 10^{28}$ photons cm^{-2} s^{-1}. Clearly this system, as used in clinical practice, is well within the multi - or multiple photon regime[11-13]. For convenience, we shall henceforth refer to this as the multiphoton regime and ignore the distinction between these in the interests of concise expression.

The relevance of the linear or low light intensity spectra to such a process is that an absorption is required to initiate this mechanism. Now all species absorb throughout the spectrum and so possess some residual absorption which will trigger multiphoton absorption[14] for any laser frequency if the laser flux is high enough. Multiphoton processes are enhanced if there is a really significant absorption at the laser wavelength as observed in a spectrophotometer. Nevertheless, the wavelength dependence of multiphoton processes is far less than that of single photon (low flux) processes as seen in a spectrophotometer. *Thus it is highly unlikely that spectrophotometric data will be a major determinant in the effectiveness of a given laser wavelength in the laser - tissue or laser - pigment interaction.*

When multiphoton absorption occurs, typical pigment ionisation energies of 10 eV (120 nm) can easily be reached (e.g. 6 photons of ruby laser light). The resultant electrons liberated from the pigment are accelerated by the electrical field (1.4×10^{6} V cm^{-1}) of the intense light strongly absorbing the remainder of the 25 ns of the laser pulse (inverse Bremsstrahlung)[9,15] so that they are multiplied considerably by multiple collisions with adjacent molecules and produce a plasma even within picoseconds. The evolution of this plasma in time and space leads to light emission, spatial expansion and heating of the target area surface in tens of nanoseconds. The expansion of the plasma leads to a recoil momentum of the target resulting in a pressure wave travelling with supersonic velocity - i.e. a shock wave. Pressures of 10^3 atmospheres (10^4 p.s.i.) are estimated to be generated[16]. Clearly these lead to significant mechanical destruction of target pigments.

It is extremely difficult to obtain the absorption spectrum of a solid at UV/visible wavelengths because the extinction coefficient is so high. For example, a 10^{-5} molar solution can exhibit optical densi-

ties of 2 over a path length of 1 cm quite readily at the wavelength of maximum absorption (i.e. such a sample is transmitting 1% of the incident light). A solid of density 2 gm cm^{-3} and molecular weight of 300 (typical of a pigment) has an effective concentration of 2 x 1000 / 300 = 6.7 molar. This should have an optical density of 2 x 6.7 x 10^5 x 6 x 10^{-4} = 800 over the 6μm of a pigment particle diameter. No spectrometer could detect such a weak signal. Even an optical density of 8 is beyond commercially available machines. Thus, such particles are essentially 100% absorbing of the light falling on them *over a very wide range of wavelengths* providing that it is not reflected or scattered. Moreover, the light will be totally absorbed very near to the surface. This has important implications for the mechanism to be discussed later. Accordingly, we have resorted to diffuse reflectance spectroscopy which is a simple technique measuring a combination of scattered and reflected light i.e. measuring the loss of light available for the absorption process. This technique allows ready comparison of the spectroscopic behaviour of different laser frequencies across the spectrum. For the purposes of comparison with liquid phase absorption spectra *only* we present some of these reflectance spectra in the form (1-reflectance).

The general characteristics of pulsed lasers used in tattoo removal are shown in Table 1. Here it is clear that, while the maximum energy densities (fluences) for these lasers do not vary greatly, the flux can vary by five orders of magnitude. Phenomena related to the flux will thus vary greatly with laser type.

TABLE 1. General Characteristics of Lasers Used for Tattoo Removal

	Nd:YAG	Alexandrite	Ruby	Dye*
Wavelength	1064 nm	755 nm	694 nm	585 nm
Energy density (max)	8 J cm^{-2}	8 J cm^{-2}	12 J cm^{-2}	8 J cm^{-2}
Typical beam diam.	3 mm	3 mm	4 mm	5 mm
Beam cross section / cm^2	0.07	0.07	0.126	0.196
Pulse width	10 ns	100 ns	25 ns	450 μs
Flux/photons $cm^{-2} s^{-1}$	$6x10^{28}$	$4x10^{27}$	$1.3x10^{28}$	$2.7x10^{23}$

* inserted here for comparison. These have been suggested for tattoo removal in the past, but are not used much for this purpose currently.

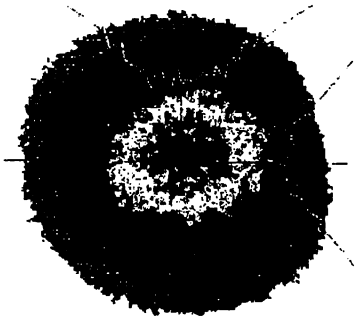

Fig. 1. The intensity profile of the Derma-Laser ruby laser. This closely approximates to the TEM_{00} profile. This was obtained with a Big Sky beam View Analyser, model BVA101 with a Cohu solid state camera No ER5002. Gaussian fit coefficients 0.9 horizontal and 0.93 vertical, diameters 2.86 mm horizontal and 2.79 vertical at 1/e points

TABLE 2. An analysis of the number, N, of treatment sessions needed for succesful removal of tattoos. Each session would consist of many laser pulses to a given site.

Laser type	Energy Density J / cm²	Pulse width /ns	Number of Sessions (N) Professional tattoos	Amateur tattoos	Reference
Ruby	6 -10	25	*13.1; 9.7; 9	*5.6; 2.5 ; 3	17
Ruby	6 - 8	40	6 -10	4 - 6	18
Nd: YAG (1064 nm)	8 -12	8	4 - 8	3 - 4	18
Nd: YAG (532nm)	(not quoted)	8	2 - 4	N/A	18
Ruby	8 - 10	28	**50% > Nd:YAG 42% = Nd: YAG best for greens	N/A	19
Nd: YAG (1064 nm)	10-14	8	8% > Nd:YAG	20% > Ruby	19
Nd: YAG (532 nm)	(not quotted, possibly 5)	8	very effective for red ink	N/A	19

* The data for 280 case studies. The first number is the mean, the second the standard deviation and the third the mode of the distribution.
** > means "better than with", = means "equally effective as".

Table 2 shows an analysis of the Number, N, of treatment sessions needed for successful removal of tattoos. Each session would consist of many laser pulses to a given site. Before analysing the clinical data, we should remember that the fluence and flux characteristics of a laser are not readily measured with any accuracy. The intensity of a laser can vary in an arbitrary manner across its diameter and so these characteristics represent an average over the laser beam cross section. If the distribution of intensity across the diameter is indeed arbitrary, this average is quite meaningless. For example, "hot spots" can readily arise, giving orders of magnitude more fluence and flux at such points than would be calculated from power meter data integrated across the full diameter. These can have a highly disproportionate effect on the decomposition mechanism initiated by such a laser. The only satisfactory route to meaningful measurements of fluence or flux is to ensure that the laser is operated with a well controlled and known intensity distribution across its diameter. The distribution of choice is usually Gaussian, being arranged by having the laser operate in TEM_{00}. It is possible to so design the cavity of a laser to produce a TEM_{00} profile [20], so that this is the simplest controlled distribution of intensity to obtain. However, energy is lost when the laser is operated in this manner and so some manufacturers will sacrifice this transverse mode quality for power. In these cases "hot spots" will undoubtedly occur and will appear randomly in position within the diameter and with time. The high quality TEM_{00} profile of the laser used in the first study[17] reported in

Table 2 is shown in Fig.1. *Without such control, comparisons of effects are unreliable.* From Table 2, it seems that the ruby laser (694 nm-red) is best for the removal of green tattoos, whereas the frequency doubled Nd:YAG (532 nm-green) is best for red ink. However, this experience contradicts the observations of the first study[17] of Table 2. *In this study, it was found that green tattoos were the most difficult of all colours to remove with the ruby laser.* Some red tattoos were removed as efficiently as e.g. blue, while others presented difficulties. This latter set of observations contradicts the simplest expectations based on considerations of low light intensity absorption spectroscopy which are that a green pigment should absorb red light and a red pigment should absorb green light. It must be remembered, of course, that for pigment mixtures metameric colour matching is possible when two colours appear the same to the eye, but differ markedly in spectral content (e.g. yellow + blue can appear the same as an appropriate mixture of green + red). Unfortunately, there can be no guarantees that tattooists will use single, pure pigments to obtain a given "red" or "green". Clearly, there is need for some simple spectroscopy to reveal the presence of such mixtures and to give an indication of the spectroscopic absorbance of a given pigment.

The purpose of the present paper is to demonstrate such a simple, reliable spectroscopy and to use it to examine the mechanism of laser induced tattoo removal based on the above clinical results.

3. MATERIALS AND METHODS

3.1. Spectroscopy

For the purpose of applying a tattoo, pigment particles of average diameter 6μm are taken up in liquids, typically proprietary mouthwash. We have found that this is not a solution, but is better described as a slurry. Indeed these pigments are essentially insoluble in any liquid, polar or non-polar. The larger particles soon precipitate, although the finer particles resist centrifuging, taking days to finally settle out. The pigments themselves are usually extremely bright and are often diluted with barium sulphate, calcium sulphate or titanium dioxide before use in tattoos. In both cases, it is clear that applying standard spectroscopic techniques to these inhomogeneous, time-varying samples presents great difficulties of interpretation and simple arguments based on the results of such studies will be unreliable.

The liquid phase "absorption" spectra were obtained on a Philips PU8720 UV/visible spectrometer using a 1 cm path length cell and freshly centrifuged preparations of pigment in mouthwash. The solid state reflectance spectra were obtained with a Spectratech diffuse reflectance attachment in Bomem DA3 Fourier transform spectrometer and referenced to filter paper (Whatman N° 1) which was found to have a flat response over the spectroscopic range of interest. The solid film was supported by the same filter paper and identical, highly reproducible, spectra were obtained irrespective of the thickness of the applied film. Solid state transmission spectra were obtained from pigment films sandwiched between two glass microscope slides in an IR Plan microscope attached to the Bomem DA3 instrument. Sites were selected where the solid film was essentially continuous and the film thickness was measured to be about 10 μm. Again, identical spectra were obtained irrespective of the site chosen in a given film. There was insufficient signal strength for this arrangement to be used to obtain the reflectance spectra. However, the percentage of light reflected in both systems is likely to be very similar, given the independence of the

spectra from film thickness in both cases. In order to check whether there was significant fluorescence present, fluorescence spectra were examined in a Perkin Elmer MPF 44 spectrofluorimeter over the complete range of excitation frequencies and no fluorescence was observed.

4. RESULTS

The interpretation of the results in a general sense, is not helped by the reticence of pigment suppliers to divulge the chemical nature of their pigments. These suppliers even refuse to acknowledge that they supply such pigments. Given the legal implications of any condition attributable to the pigments this reticence is understandable.

4.1. Identity of the Pigments

The pigments used in the current study were subjected to Energy Dispersive X-ray Fluorescence, EDXRF, analysis (Oxford-Tennelec Nucleus, Si/Li detector, 170 eV resolution at 5.9 ke V,^{109} Cd source) and Powder X-ray diffraction in order to acquire some knowledge of their chemical nature. It is out of the question to exactly identify these pigments, since they are undoubtedly mixtures and probably impure compounds. Nevertheless, these studies were quite revealing. The X-ray diffraction conclusively proved that the white pigment was titanium dioxide and that the blue was copper phthalocyanine .The green pigment seemed to be a mixture of TiO_2 and a copper compound, but with a high bromine content.

We deduce that this probably indicated the presence of a brominated copper phthalocyanine plus possibly other orange pigments. The yellow, orange and red pigments, which present similar reflectance spectra, are all heavily chlorinated pigments, the yellow and orange being diluted with calcium sulphate. Strangely, the light red pigment does not contain chlorine but is lightened by addition of the expected TiO_2. In fact the reflectance spectra, as used in this study, provide a simple and valuable diagnostic aid to determine whether pigment samples are of the same origin. The brown pigment was essentially two forms of titanium dioxide (anatase and rutile) together with some organic pigment.

4.2. Liquid phase spectra

Given the inhomogeneous nature of the liquid phase spectra in the visible wavelength range, these were not used as a basis for any deduction. They are shown with the accompanying solid phase spectra for comparison. In the case of the red pigment (Fig. 2) solid phase (1-reflectance) spectra and liquid phase "absorption" spectra yield similar results, but in the case of the blue and green pigments (Figs.3, 5 and 6) the liquid phase spectra show a broad structure which is quite different from that seen for the solid. The scattering properties of the solid particles suspended in the liquid will be quite different from those of a film of solid particles as found in a tattoo, so that such differences are not surprising. Accordingly, such spectra are considered to be quite useless in assessing the behaviour of the solid pigment to laser radiation.

4.3. Solid State Reflectance Spectra

The reflectance spectra of the solid films may be classified into two groups. Pigments through the range from red to yellow and brown yield spectra similar to the red pigment as shown in Fig.4. The blue

and green pigments, however, show distinctive features in the infrared region (Fig.5). In Figs. 6 and 7, the solid phase spectra shown are calculated from 100% less the percentage of reflected light, scattered light and light transmitted by the sample. This is simply for the purpose of approximate comparison with the liquid phase spectra which are in the absorbance mode. Given the high extinction coefficient expected for such pigments, it is most likely that the observed transmitted light is transmitted indirectly by a series of reflections from particle facets in the thickness of the rather open film.

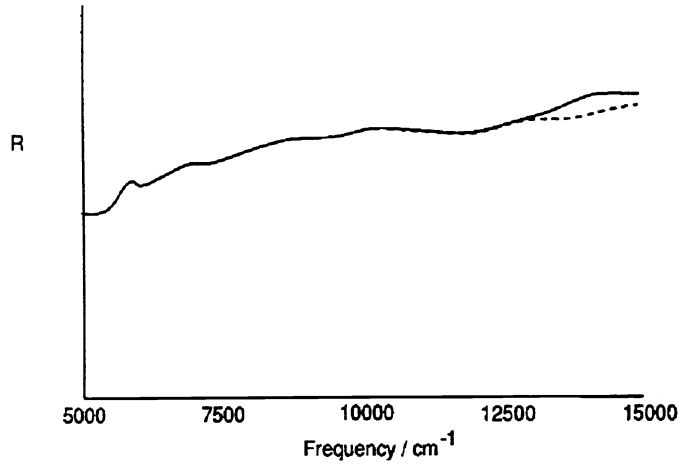

Fig. 2. Red pigment, solid line = (1-solid phase reflectance) spectrum, dotted line = liquid phase "absorbance" spectrum, (both in arbitrary units).

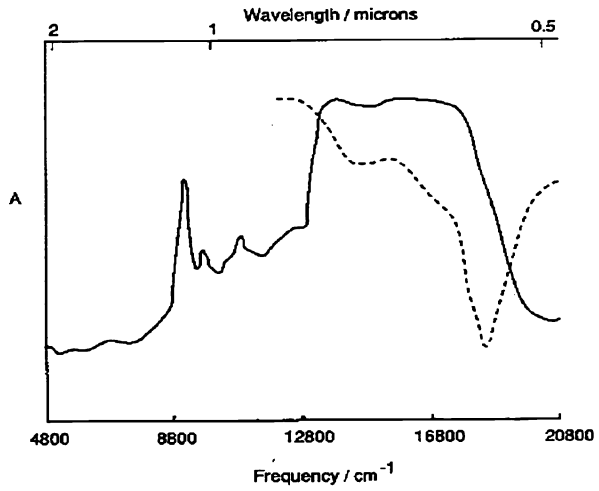

Fig. 3. Blue pigment, solid line = (1-solid phase reflectance) spectrum, dotted line = liquid phase "absorbance" spectrum, both in arbitrary units.

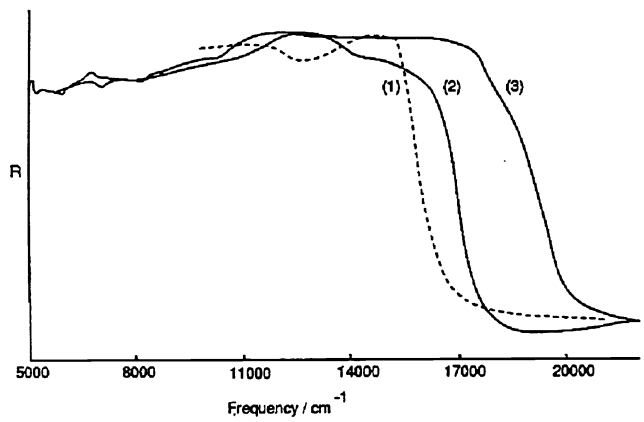

Fig. 4. Reflectance spectra of (1) = light red pigment, (2) = Red Pigment, (3) = yellow pigment, all in arbitrary units.

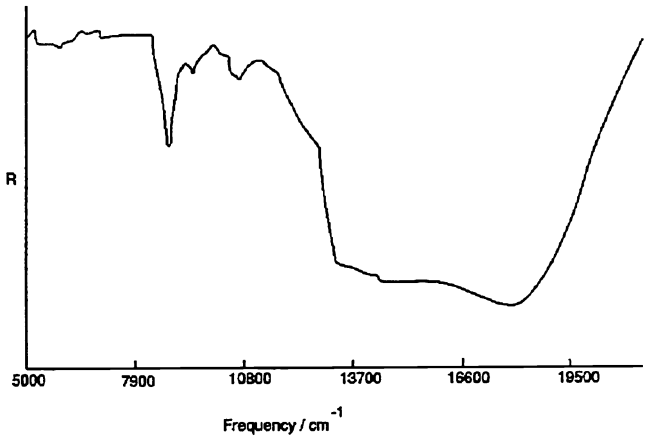

Fig. 5. Reflectance spectrum of blue pigment in arbitrary units.

In this case the transmitted light is simply the forward reflected light. There is little difference in the spectrum whether the transmitted component is included or not, although there is a slight red shift in the absorbance calculated by the former method and such a shift can only be due to a significant absorbance component affecting the transmitted light. The figures for absorbances estimated this way must be in arbitrary units, since the spectrometer will fail to collect all the scattered light by some degree which varies with each sample.

If we consider the reflectance spectra of the blue and green pigments in Fig. 7, remembering that these represent the light lost by reflection and backscattering, it is clear that the loss of light is low and similar for both pigments at the ruby laser wavelength. The units shown are exactly as produced by the spectrometer. However, differences in surface texture may change these by around 0.1 reflectance units. Thus the behaviour of these pigments to this laser should be similar. If these pigments behave differently, it is not, therefore, due to the spectroscopic characteristics of the compounds, but to some other factor. Given that the ionisation potential of these pigments will also be closely similar, the shock wave generation following multiphoton ionisation is expected to be similar. Closer investigation [21] of the two pigments reveals that the particle size distribution is different, however. The green pigment contains particles up to 200 μm diameter while the blue particles have a maximum diameter of 100 μm. Since the blue and green pigment spectra are similar in the ruby laser regime, however, the effect of the skin and the tissue/pigment interface as against the air/pigment interface will be common to both, we attribute the different behaviour of these two pigments to the ruby laser to this difference in particle size. In amateur tattoos the pigment

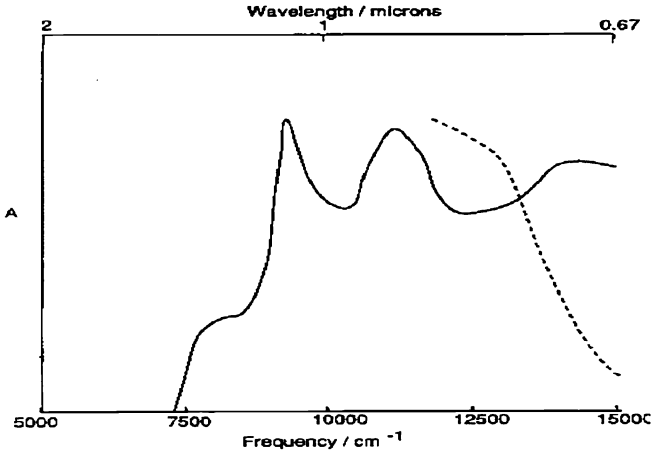

Fig. 6. Green pigment, solid line = (1-solid phase reflectance) spectrum, dotted line = liquid phase "absorbance" spectrum, both in arbitrary units.

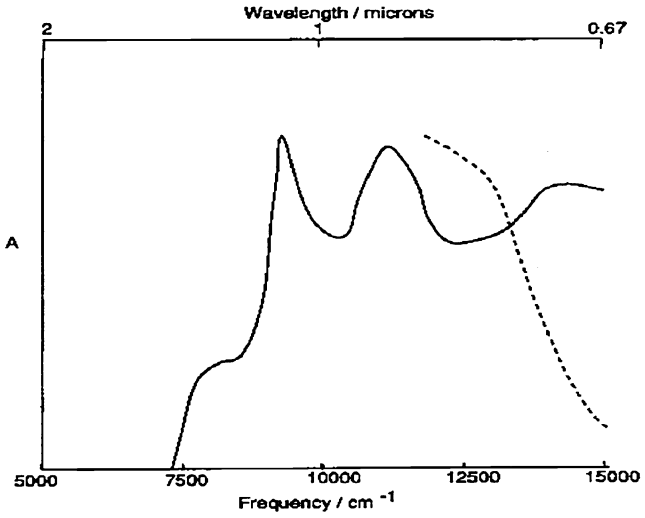

Fig. 7. Reflectance spectra of the blue (solid line) and green (dotted line) pigments referenced to an aluminum mirror. The vertical lines indicate laser wavelengths,

(a) = Nd:YAG, (b)=Alexandrite, (c)=ruby, (d)=frequency doubled Nd: YAG.

has been found to be largely extra-cellular located in "pools" in the mid to deep dermis. Professional tattoo work, however, lodges pigment both extra-and intra-cellularly, the latter being contained in the cytoplasm of macrophages. This is probably why professional tattoos are more difficult to remove [22,23]. Additionally, the green pigment is not a pure compound, but, as deduced above, probably contains a mixture of brominated copper phthalocyanine and other organic pigments. Unlike the pure, blue copper phthalocyanine, this mixture will not grind to such a fine powder, but will tend to form a "paste" and give the larger aggregates as observed.

Likewise, from fig. 7 it is clear that both alexandrite and ruby laser light are reflected similarly by these pigments and thus similar behaviour would be expected from low light intensity arguments. The alexandrite laser is found to be less effective[24] than the ruby[25], however, and this must therefore be due to the difference in flux (W cm^{-2}). Not only must the energy (J) be considered in such a comparison, but the pulse width and irradiated area are also vitally important, all these being involved in the calculation of the flux (see above). Multiphoton processes are flux driven not fluence driven, and so such a mechanism is most probably operating in the tattoo removal process as predicted from the calculations shown above.

5. DISCUSSION

"Absorbance" spectra of pigments slurried in liquid have been shown not to be true absorbance spectra for typical compounds and from their insolubility in essentially any solvent. It has also been shown above that the absorbances of all pigments throughout the visible spectrum may be considered to be extremely strong even at quite large wavelength separations from the centre of the transitions. These spectra are therefore disregarded as useful diagnostics either for the identification of pigments as similar or for predicting their spectroscopic behaviour in laser assisted tattoo removal.

Solid state spectra have been obtained by a simple diffuse reflectance technique and in transmission mode under a microscope. In the latter experiments, the "transmitted" light closely corresponds, spectroscopically, to reflected light. Additionally, there were no visible direct paths through the sample. It is therefore deduced that this "transmitted" light permeates the sample by multiple reflection in voids within the sample thickness and is not light remaining after true absorption. This is expected from the estimation of likely extinction coefficients for such materials.

Our interpretation of the reflectance experiments is that these give a reasonably accurate measure of the loss of light energy at the surface of the solid pigment. This measure will be valid both across the wavelength range and between different pigments, although in the latter case, sample preparation can lead to minor (<0.1 reflectance units) irreproducibilities. Given the enormous absorption coefficients in the visible spectrum expected for all these pigments from red through to blue and that their colour as perceived by the eye is directly related to their reflectance spectra as we obtain them, considerations of their colour in terms of their relative absorbance are certainly irrelevant. Of course, reflectance and absorbance are related, but the extremely high absorbance of all these solids at particle sizes representative of tattoo practice implies that they will differ in this respect less sharply, both as a function of wavelength and in their depth of surface penetration of the light, than would be expected. In all cases this will be extremely small, i.e., all light absorption of all colours of pigment will occur essentially within <1 μm of the surface. This process will, at sufficiently high *flux*, lead to multiphoton absorption, ionisation, plasma formation, followed by shock wave production and mechanical, pressure-wave-induced breakdown of the pigment

particle. The flash of light observed clinically is almost certainly indicative of emission of highly excited states in this plasma and not of a mechanism where such states are excited thermally. For the reasons given above, the wavelength dependence of this mechanism is much less sensitive than might be expected from the usual characteristics of absorption spectra of dyes.

In all experiments a comparatively fine dividing line exists between the onset of this mechanism for the pigment and the operation of this mechanism in the overlying tissues above the tattoo. If the flux is too high, the skin will be disrupted also. If the flux is too low, little or nothing will happen to the pigment or the skin. The alexandrite laser is less effective than the ruby quoted here, almost certainly because its pulse width is around 75-100 ns compared with the 25 ns of the ruby. For equal irradiated areas and pulse energies, this means that the alexandrite flux is 4 times less than that of the ruby.

Since this multiphoton mechanism is highly non-linearly dependent on the laser flux, the control of the laser beam intensity profile is of great importance. Failure to ensure such a stable profile will lead to random production of unusually high flux zones in the laser cross-section. These are very likely to initiate multiphoton processes in the skin and cause unwanted disruption, possibly leading to scarring. To minimise scarring, the flux on the beam axis must never exceed the value which allows multiphoton absorption to occur in the skin tissue. This can only be guaranteed if the laser operates in the TEM_{00} mode.

The mechanism explains also the vast superiority of the Q-switched laser over the cw laser. Multiphoton processes and their attendant shock wave cannot occur with cw radiation. Only truly thermal processes will occur, leading in effect to a burn in the traditional sense. The effect of the absorbance spectrum of the pigment will be greater in such a case, but the loss factors as measured by our reflectance spectra are still very relevant in assessing the differential effects of various lasers and pigments. The pigment will still be essentially totally absorbing at its surface.

In applications requiring the thermally induced coagulation of blood vessels, lasers with pulse lengths in the milliseconds regime are predicted to be best. This is because shock wave induced particle breakdown is not required in these cases. The heating of a blood vessel depends on the laser *flux* again, because now the temperature reached by the blood in the vessel depends on the fine energy balance[26] between the input laser flux and the thermal diffusivity of the vessel. This latter depends, amongst other parameters, upon the inverse of the square of the radius of the vessel. Thus, there will be a range of vessel diameters below which a given cw laser is ineffective, due to too rapid heat removal, and above which the temperature rise will be excessive, leading to unfortunate effects. In this context it should be noted that too high a repetition rate of the long laser pulses, applied to the same spot, will again lead to excessive temperature rise, because the thermal diffusivity of tissue (essentially that of water) is such that seconds must elapse before ambient temperature is reached (within 1%) in treated tissue. Being controlled by these kinetic factors, there is a great tendency for temperature to integrate with time if such long periods are not allowed. In the tattoo removal experiments all the applied energy is ultimately degraded to heat and, for the same reasons as just discussed, the Q-switched pulse repetition rate should not be much above 1 Hz at the same spot [27,28]. Indeed there is some evidence that patients treated with the higher repetition rate lasers do show more scarring than when low repetition rate systems are used.

6. ACKNOWLEDGMENTS

Professor Konstadinos Siomos wishes to thank the EU (Comett programme) for their financial support. The assistance of Professor G. Kostakis, Dr. G.A. Alevizos and Dr. N. Kallithrakas-Kontos in obtaining the X-ray diffraction and fluorescence spectra is gratefully acknowledged.

7. REFERENCES

1. M.L. Kohlbarsht (Ed.), "*Laser Applications in Medicine and Biology*", 1-3, Plenum Press, N.Y., (1971-1977).
2. K. Siomos, (Ed.), "*Lasers in Medicine*", Pelekanakis Press, Chania, Greece, (1988).
3. J.A.S. Carruth and McKenzie A.L., "*Medical Lasers-Science and Clinical Practice*", Adam Hilger Ltd., Bristol, (1986).
4. G.I. Mueller and Berlien H.P. (Eds.), "*Safety and Laser Tissue Interaction*", Ecomed, Berlin, (1989).
5. K. Siomos (Ed.), "*Lasers in Basic Sciences, Engineering and Medicine*", The Institute of Materials Structure and Laser Physics, Chania, Greece, (1991).
6. K. Siomos (Ed.), "*Lasers in Science, Technology and Life*", The Institute of Materials Structure and Laser Physics, Series in Laser Applications No. 4, Chania, Greece, (1994).
7. R.R. Anderson and Parrish I.A., "The Optics of Human Skin", J. Invest. Dermat., (1981): 77: 13-19.
8. A.J. Welch and Motamedi M., "Interaction of Laser Light with Biological Tissue" , in "*Laser Photobiology and Photomedicine*" (Martellucci S. and Chester A.N., Eds.), N.Y.: Plenum Press: (1985): 29-53.
9. K. Siomos, "Laser Light Tissue Interaction - On the Mechanism of Optical Breakdown" in "*Future Trends in Biomedical Applications of Lasers*" (Svaasand L.O. Ed). SPIE:1525: (1991):154-161.
10. R.T. Bailey and Cruickshank F.R., "Infrared Laser Photochemistry", Royal Society of Chemistry: (1987): Annual Reports A: 49-97.
11. K. Siomos, "High Order Effects and Processes in the Laser Interaction with organic Molecules" in "*Lasers in Medicine*" (Siomos K. Ed.), Chania, Greece: Pelekanakis Press: (1988): 50-73.
12. K.Siomos, "Laser Non-Linear Spectroscopy of Polyatomic Molecules in the Liquid phase and Me dium Dependent Processes" in "*Lasers in Atomic, Molecular and Nuclear Physics*" (V.S. Letokhov, Ed.), London, World Scientific: (1987): 259-278.
13. K. Siomos, "Laser Multiphoton Ionisation Spectroscopy of Polyatomic Molecules" in "*Chemical Analysis of Polycyclic Aromatic Compounds*", (T. Vo-Dihu, Ed.), N.Y., J. Wiley and Sons: (1989): 263-325.
14. C.A. Puliafito and Steiner R.F. IEEE J. Quant. Electronics: (1984): QE20: 1441-1448.
15. J.F. Ready, "*Effects of High Power Laser Radiation*", N.Y. Academic Press: (1971).
16. J.G. Fujimoto, Lin W.Z., Ippen E.P., Pulifito C.A., and Steiner F.R., Invest. Opthal and Visual Science: (1985): 26: 1771-1777.

17. M.J. Murphy unpublished data.

18. S.L. Kilmer and Anderson R.R., "Clinical use of the Q-switched ruby and Q-switched Nd: YAG (1064 nm and 532 nm) lasers for treatment of tattoos"2, J. Dermatol. Surg. Oncol.: (1993): 19: 330-338.

19. R. Geronemus and Levine V., "Tattoo Removal with the Q-switched ruby laser and the Nd: YAG laser": slide programme 260", Am. Soc. Laser Medicine and Surgery, Annual Meeting, New Orleans, (1993).

20. C.G.B. Garett, "*Gas Lasers*": N.Y.: McGraw Hill: (1967).

21. C.A. Vance, "*An Investigation into Q-Switched Ruby Laser Treatment of Tattoos*": MSc Thesis: Glasgow: University of Strathclyde: (1985): p52.

22. P. MacLeod, "*Selective Absorption in the Laser Treatment of Tattoos and Port Wine Haemangiomas*": PhD Thesis: Glasgow: University of Strathclyde: (1984).

23. A. Ritchie, "*Q-Switched Ruby Laser Treatment of Blue-Black Tattoos*": PhD Thesis" Glasgow: University of Strathclyde: (1982).

24. Fitzpatrick R.E., Goldman M.P. and Ruiz-Esparza J., "Use of alexandrite laser (755 nm, 100 ns) for Tattoo Pigment Removal in an Animal Model", J. Amer. Acad. of Dermatology: (1993): 28: 745-750.

25. W.H. Reid, Miller D., Murphy M.J., Paul J.P. and Evans J.H. "Q-Switched Ruby Laser Treatment of Tattoos; 9a- Year Experience", British J. of Plastic Surgery: (1990): 43: 663-669.

26. R.T. Bailey, Cruickshank F.R., Pugh D., Guthrie R., Johnstone W., Mayer J. and Middleton K. "Thermal Effects in Infrared Photochemistry and Energy Transfer Experiments", J. Chem. Phys.: 77, (1982): 3453-3457.

27. S. Venkatesh, Guthrie S., Bailey R.T., Cruickshank F.R., Foulds W. and Lee W. "Thermal Lens Measurements in Cornea", British J. Ophthalmology: (1981): 69: 92-95.

28. S. Venkatesh, Guthrie S., Foulds W., Lee W., Bailey R.T., Cruickshank F.R., "In Vitro Studies with a Pulsed Nd: YAG Laser", British J. Ophthalmology: (1981): 69 : 86-91.