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RESONANCE AS NEW METHOD IN DETERMINING THE AGE OF PAINTS

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Abstract: In this work the mechanism of resonance is proposed as the way for determining of paint age, by application of this method. This method consists in accelerated paint ageing on the basis of resonance. Measuring is concerned with humidity of paint and it is a general method since water molecules are present in every material. The molecules of water have random distribution. They oscillate in shallow potential wells so that they can be ejected from paint with low energy quanta, thus decreasing the paint humidity by evaporation process. The high energy quanta accelerate this process of the paint ageing. Since water molecule is mechanical oscillator it can be turned into resonance by application of mechanical periodical field, but since it is electric dipole it can be even more conveniently turned into resonance with periodic electric field.

Keywords: resonance method, accelerated paint ageing.

1. INTRODUCTION

The age of paint is one of important forensic problems since a number of forgeries of artistic paints permanently increases. There are many attempts in solving this problem. One of ideas is accelerated drying of paint. This work is devoted to that problem.

We start from the fact that all paints contain some percent of molecules H_2O and that their humidity decreases in time [1]. The humidity level is one of the criterions for determining of paint age. Accelerated decrease of humidity can be realized by resonance effect, since resonant energy is proportional to the square of time [2]. The molecules H_2O are strong dipoles and therefore they can turn into resonance state, both by mechanical and electrical resonators.

In the first part of this work we shall shortly expose elements of mechanical and electrical resonance. In the second part these results will be used for determining of paint age by mechanism of accelerated drying.

2. MECHANICAL AND ELECTRICAL RESONANCE

The mechanical resonance will be studied by quantum approach. We shall consider one dimensional quantum oscillator with Hamiltonian [3]

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{1}$$

in periodical field defined by the Hamiltonian:

$$H_{\text{int}} = -vp\cos\Omega t \tag{2}$$

In these formulas m is mass of oscillator, x is coordinate, p is the momentum, ω is internal frequency of oscillator, Ω is the frequency of external field and v is proportionality factor having velocity dimension. Using commutation rule $[x, p] = i\hbar$ [4-6], we obtain the following equation of motion for coordinate x

$$\dot{x} = \frac{p}{m} - v\cos\Omega t \tag{3}$$

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Differentiating (3) with respect to time, we obtain

$$\ddot{x} = \frac{1}{m}\dot{p} + v\Omega\sin\Omega t \tag{4}$$

Since $\dot{p} = \frac{1}{i\hbar}\left[p,\left(H_0 + H_{\text{int}}\right)\right]$ we have $\dot{p} = -m\omega x$. Putting this into (4) we obtain non homogenous differential equation for coordinate *x*:

$$\ddot{x} + \omega^2 x = v\Omega\sin\Omega t \tag{5}$$

The solution of (5) we are looking for in the form [7,8]:

$$x = x_h + A\sin\Omega t \tag{6}$$

where $x_h = C_1\cos\omega t + C_2\sin\omega t$ is the solution of homogenous differential equation:

$$\ddot{x}_h + \omega^2 x_h = 0 \tag{7}$$

Inserting initial conditions

$$x(0) = 0\ ;\ \dot{x}(0) = L\Phi \tag{8}$$

into general solution of (5), which is of the form:

$$x = C_1\cos\omega t + C_2\sin\omega t + A\sin\Omega t \tag{9}$$

we obtain the following values for constants C_1 and C_2:

$$C_1 = 0\,;\ C_2 = \frac{L\Phi}{\omega} - \frac{1}{\omega}\frac{v\Omega^2}{\omega^2 - \Omega^2} \tag{10}$$

Consequently, the solution (9) becomes

$$x(t) = \frac{L\Phi}{\omega}\sin\omega t + \frac{v\Omega}{\omega}\frac{\omega\sin\Omega t - \Omega\sin\omega t}{\omega^2 - \Omega^2} \tag{11}$$

If external frequency Ω tends to internal one ω, we obtain the resonant value for coordinate *x*.

$$x_R = \lim_{\Omega\to\omega} x(t) \tag{12}$$

By means of L'Hospital's rule [9,10] we find

$$x_R(t) = \left(\frac{L\Phi}{\omega}\sin\omega t - \frac{v}{2\omega}\right)\sin\omega t - \frac{vt}{2}\cos\omega t \tag{13}$$

For $t >> 1$ the second term in (13) becomes dominant, so we can write

$$x_R(t) \approx -\frac{vt}{2}\cos\omega t \tag{14}$$

From (14) we have

$$\dot{x}_R(t) = -\frac{v}{2}\cos\omega t + \frac{v\omega t}{2}\sin\omega t \approx \frac{v\omega t}{2}\sin\omega t \tag{15}$$

Putting (14) and (15) into (1) we find that resonant energy of mechanical oscillator is given by:

$$E_R(t) = \frac{1}{8}mv^2\omega^2 t^2 \tag{16}$$

The problem with mechanical resonant lies in the fact that elongation *x* is proportional to *t* (see formula (14)) so that after too long *t* we can go out from elasticity domain [2].

This problem does not appear in the case of electrical resonance which could be realized in *LC* circuit connected to periodical voltage $u(t) = U_0\cos\Omega t$.

The voltage equation [11,12]

$$L\frac{di}{dt} + \frac{1}{C}\int_0^t i\,dt = U_0\cos\Omega t \tag{17}$$

where i is current, after differentiating with respect to *t* becomes

$$\frac{d^2 i}{dt^2} + \omega^2 i = -\frac{U_0\Omega}{L}\sin\Omega t \tag{18}$$

We are looking for general solution of (18) in the form

$$i(t) = i_h(t) + A\sin\Omega t \tag{19}$$

where $i_h(t)$ is solution of homogenous part of (18).

For initial conditions $i(0) = 0\,;\ \frac{di}{dt}(0) = I_0\Phi$, we obtain

$$C_1 = 0\,;\ C_2 = \frac{I_0\Phi}{C_0} + \frac{U_0\Omega^2}{L\omega}\frac{1}{\omega^2 - \Omega^2} \tag{20}$$

Consequently, the solution (19) is

$$i(t) = \frac{I_0\Phi}{\omega}\sin\omega t + \frac{U_0\Omega}{L\omega}\frac{\Omega\sin\omega t - \omega\sin\Omega t}{\omega^2 - \Omega^2} \tag{21}$$

The resonance current $i_R(t)$ is given by:

$$i_R = \lim_{\Omega\to\omega} i(t) = \left(\frac{I_0\Phi}{\omega} - \frac{U_0}{2L\omega}\right)\sin\omega t + \frac{U_0 t}{L}\frac{\cos\omega t}{2}. \tag{22}$$

After sufficiently long time we can write

$$i_R \approx \frac{U_0}{2L}t\cos\omega t\,. \tag{23}$$

The resonant voltage becomes:

$$u_R(t) = U_0\cos\omega t \tag{24}$$

and, consequently, the resonant power is given by

$$P_R \approx \frac{U_0^2}{2L}t\cos^2\omega t\ . \tag{25}$$

For resonant energy we have:

$$E_R = \int_0^t dt P_R(t) \approx \frac{U_0^2}{8L} t^2 \tag{26}$$

It is seen that the electrical resonance, as well as the mechanical one, gives energies proportional to square of *t*.

3. WATER MOLECULES IN PAINT. DIPOLE PHONONS

The molecules of water have random distribution. They oscillate in shallow potential wells so that they can be ejected from paint with low energy quanta. It is the reason for decrease of paint humidity by evaporation process. The high energy quanta accelerate the process of ejecting water molecules from the paint. On this basis, it becomes obvious that the increase of energy of water molecules accelerates the paint ageing. As water molecules have random distribution, the dipoles of water are not bounded by dipole-dipole interactions [13,14]:

$$W_{\vec{n},\vec{m}} = \frac{\vec{d}_{\vec{n}}\vec{d}_{\vec{m}}}{|\vec{n}-\vec{m}|^3} - 3\frac{\left[\vec{d}_{\vec{n}}(\vec{n}-\vec{m})\right]\left[\vec{d}_{\vec{m}}(\vec{n}-\vec{m})\right]}{(\vec{n}-\vec{m})^5} \tag{27}$$

where $\vec{d}$ is dipole while $\vec{n}$ and $\vec{m}$ are crystal lattice vectors.

On the other hand, every isolated dipole can rotate about some axis producing oscillation quanta. Due to the random distribution of H_2O dipoles it is more realistic to consider the system of water molecules in paint as the system of independent physical pendulums. The quanta of these dipole oscillation we shall call dipole phonons, in contrast to usual "optical phonons" since the last can be confused with optical branches of phonons in the crystal with complex lattice.

Force momentum *M* is given by the following equation:

$$M = F_a L = mgL\sin\theta \tag{28}$$

Since the oscillations are small we shall take $\sin\theta \approx \theta$ and due to opposite sign of vectors $d\vec{\theta}$ and $\vec{M}$ we write

$$M = -I\ddot{\theta} \tag{29}$$

where *I* is inertial momentum of dipole H_2O. Consequently, (28) reduces to:

$$\ddot{\theta} + \omega^2\theta = 0 \tag{30}$$

where

$$\omega^2 = \frac{mgL}{I} \tag{31}$$

For H_2O molecule we assume cylindrical form with length *D* and homogenous density ρ. For rotation axis we shall take *z* axis.
So we have [20]

$$I = \rho\int_0^D dz\int_0^{2\pi} d\varphi\int_0^R dr r^3 = \frac{1}{2}mR^2 \tag{32}$$

After substitution of (32) into (31) we obtain (due to the homogenous density ρ it follows that $D = 2L$):

$$\omega = \frac{1}{R}\sqrt{gD} \tag{33}$$

Taking $D = 10^{-10}m$ and $R = 10^{-11}m$ we find that energy of dipole phonons is

$$E = \frac{\hbar}{R}\sqrt{gD} = 3{,}133\cdot 10^{-28} J \tag{34}$$

Since H_2O molecule is mechanical oscillator it can be turned into resonant state by application of mechanical periodical field but also, since it is dipole, it can be turned into resonant state with periodical electric field $\vec{\varepsilon}$ [18]. Since $\vec{\varepsilon}$ is electromagnetic wave its energy is $E_\varepsilon = \hbar ck = \frac{hc}{\lambda}$, wherefrom $\lambda = \frac{hc}{E_\varepsilon}$. The resonance between dipole phonons and these electromagnetic waves requires $\lambda = \frac{2\pi cR}{\sqrt{gD}} \sim 600\text{m}$. It means that H_2O dipoles can be turned into resonant state by radio waves with wavelength higher than 600m.

The solution of rotation angle equation (30) is given by:

$$\theta(t) = C_1\cos\omega t + C_2\sin\omega t\,. \tag{35}$$

Taking initial conditions $\theta(0) = 0$ and $\dot{\theta}(0) = \theta_0\Phi$, we obtain the expression for rotation angle of nonresonant dipole phonons:

$$\theta(t) = \theta_0\frac{\Phi}{\omega}\sin\omega t \tag{36}$$

Now we shall look for rotation angle energies of dipole phonons which are in resonance with external periodical field. The angle acceleration of this field we shall take in the form $F\Psi\sin\Omega t$, where *F* has dimension square of frequency.

Consequently, the equation (30) transforms into nonhomogeneous equation [19]:

$$\ddot{\theta} + \omega^2\theta = F\,\Psi \sin\Omega t\,. \tag{37}$$

Taking the same initial conditions as earlier, i.e. $\theta(0) = 0$ and $\dot{\theta}(0) = \theta_0\Phi$ we obtain the solution of (37) in the form:

$$\theta = \theta_0 \frac{\Phi}{\omega}\sin\omega t + \frac{F\ \Psi}{\omega}\ \frac{\omega\,\sin\Omega t - \Omega\,\sin\omega t}{\omega^2 - \Omega^2} \tag{38}$$

The oscillator comes into resonant state when $\Omega \to \omega$. It means that

$$\theta_R = \lim_{\Omega\to\omega}\theta \tag{39}$$

Putting in (38) $\Omega \to \omega$, and using L'Hospital's rule, we find

$$\theta_R = \left(\theta_0\frac{\Phi}{\omega} + \frac{F\,\Psi}{2\omega^2}\right)\sin\omega t - \frac{1}{2}\frac{F\,\Psi}{\omega}\,t\cos\omega t\,. \tag{40}$$

After a long time, the second term in (40) becomes dominant. Therefore, in further, it will be used the approximate formula

$$\underset{t\rangle\rangle 1}{\theta_R} \approx -\frac{1}{2}\,\frac{F\,\Psi}{\omega}\,t\cos\omega t\,. \tag{41}$$

In order to find resonant energy of dipole phonons we shall determine angle velocity $\dot{\theta}$. Differentiating (41) with respect to time and leaving only the term proportional to time we have

$$\dot{\theta} = F\,\Psi\,t\sin\omega t\,. \tag{42}$$

Resonant energy is given by the formula

$$E_R = \frac{1}{2}I\,\dot{\theta}_R^2 + \frac{1}{2}I\omega^2\,\theta_R^2\ . \tag{43}$$

Substituting (41) and (42) into (43) we obtain

$$E_R = \frac{1}{8}IF^2\,\Psi^2\,t^2\,. \tag{44}$$

The nonresonant energy can be determined by using formula (36), with $\theta(t) = \theta_0\,\frac{\Phi}{\omega}\sin\omega t$, wherefrom it follows $\dot{\theta} = \theta_0\Phi\cos\omega t$. Putting θ and $\dot{\theta}$ into the formula similar to (43) we obtain nonresonant energy of dipole phonons:

$$E = \frac{1}{2}I\theta_0^2\,\Phi^2 \tag{45}$$

Comparing (44) to (45) we can conclude that after long time the resonant energy E_R, which is proportional to t^2 is noticeably higher than nonresonant energy *E*.

Now we can explain how accelerated ageing can be used for determining the age of the paint sample.

As it was said earlier the molecules of water have random distribution in paint and oscillate in shallow potential wells. Relatively small energies can cause their evaporation leading to the paint ageing. The higher energies accelerate evaporation and, consequently, accelerate growing the paint ageing. As the measure of velocity of the paint ageing, one can take the value of the change of number of molecules H_2O in time. This change can be determined by very popular semi empirical law: the change of number of particles *N* in time is proportional to number of particles with negative sign. Proportionality factor, between $\frac{dN}{dt}$ and *N*, is proportional to the energy of particles (this approach is mostly used in the theory of radioactive decay) [20-23].

If dipoles H_2O are in nonresonant state, then accordingly we can write

$$\frac{dN}{dt} = -K\,N(t) \tag{46}$$

where $K \sim E = \frac{1}{2}I\theta_0^2\,\Phi^2$. From (46) it follows

$$N(t) = N_0\,e^{-K_0\,t} \tag{47}$$

where N_0 is number of molecules of H_2O in the moment $t = 0$.

If dipoles H_2O are in resonant state, we can write

$$\frac{dN_R}{dt} = -K_R(t)\,N_R(t) \tag{48}$$

where $K_R(t) \sim E_R(t) = \frac{1}{8}IF^2\,\Psi^2\,t^2$, and shortly

$$\mathrm{K_R(t) = 3K_{0R}}t^2 \tag{49}$$

Putting (49) into (48) and solving differential equation, we obtain number of molecules of H_2O which remain in paint after time *t*:

$$N_R(t) = N_0\ e^{-K_{0R}\,t^3} \tag{50}$$

Constants K_0 and K_{0R} must be determined empirically. Measuring $N(t_1)$ and $N(t_2)$ where $t_2 > t_1$ and $N(t_2) < N(t_1)$, we obtain in accordance with (47):

$$K_0 = \frac{\ln N(t_1) - \ln N(t_2)}{t_2 - t_1} \quad (51)$$

In the same manner, we obtain in accordance with (49):

$$K_{0R} = \frac{\ln N_R(t_1) - \ln N_R(t_2)}{t_2^3 - t_1^3}. \quad (52)$$

Determining of more realistic values K_0 and K_{0R} requires set of n measurements which give values $(K_0^1, K_0^2, \cdots, K_0^n)$ and $(K_{0R}^1, K_{0R}^2, \cdots, K_{0R}^n)$. The values of K_0 and K_{0R} would be taken as arithmetical mean values of the quoted numbers, i.e.:

$$K_0 = \frac{1}{n}\left[K_0^{(1)} + K_0^{(2)} + K_0^{(3)} + \cdots + K_0^{(n)}\right] \quad (53)$$

and

$$K_{0R} = \frac{1}{n}\left[K_{0R}^{(1)} + K_{0R}^{(2)} + K_{0R}^{(3)} + \cdots + K_{0R}^{(n)}\right]. \quad (54)$$

Finally, we can describe the procedure of determining of the age of some paint sample. We must make the identical sample with fresh paint (the examined sample was fresh painted in the moment when it was made). This fresh painted sample has to be put in resonant state by mechanical or electrical resonance, and humidities of both samples have to be measured [24,25]. After a time τ the humidities of both samples become equal, which means that after time interval τ the following equality is valid:

$$N_R(\tau) = N(\tau + T) \quad (55)$$

where T is the age of examined sample.

From the formula (55) it follows:

$$T = \frac{K_{0R}}{K_0}\tau^3 - \tau \quad (56)$$

Now we shall give some illustrative examples:

1. If $K_{0R} = K_0$ and humidities become equal after τ = 1800 s, the age of sample is T = 185 years, while for τ = 600 s the age of sample is T = 6.5 years.

2. If $\frac{K_{0R}}{K_0} = \frac{1}{10}$, then for τ = 1800 s the age of sample is T = 18.5 years, while for τ = 600 s the age of sample is 250 days.

3. For $\frac{K_{0R}}{K_0} = \frac{1}{100}$, then for τ = 1800 s the age of sample is T = 1,85 years, while for τ = 600 s the age of sample is 25 days.

4. CONCLUSION

The advantages of proposed method for determining the age of paint are:

1. All paints possess some percent of molecules H_2O.

2. Molecules H_2O are dipoles and due to this they can be put to resonant state by mechanical and electrical resonances.

Disadvantage of this method is the fact that here was considered the case of dipole phonons corresponding to rotation of dipole about axis. The more general approach would be taking into account rotation of dipoles about point, where two Euler's angles change in time.

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РЕЗОНАНЦИЈА КАО НОВИ МЕТОД ЗА ОДРЕЂИВАЊЕ СТАРОСТИ БОЈЕ

Сажетак: У овом раду предложен је механизам резонанције као начин за одређивање старости боје, применом ове методе. Овај метод се састоји у убрзаном старењу боје на основу резонанције. Мерење се односи на влажност боје и то је општа метода, јер су молекули воде присутни у сваком материјалу. Молекули воде имају случајну дистрибуцију. Они осцилују у плитким потенцијалним јамама тако да се могу избацити из боје са квантима ниске енергије, чиме смањују влажност боје процесом испаравања. Квант високе енергије убрзава овај процес старења боје. Будући да је молекул воде механички осцилатор, може се довести у резонанцију применом механичког периодичног поља, али пошто је електрични дипол, може се још повољније довести у резонанцију с периодичним електричним пољем.

Кључне ријечи: метод резонанције, убрзано старење боје.

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